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DEVELOPMENT OF A CHEMICAL DENITRIFICATION PROCESS

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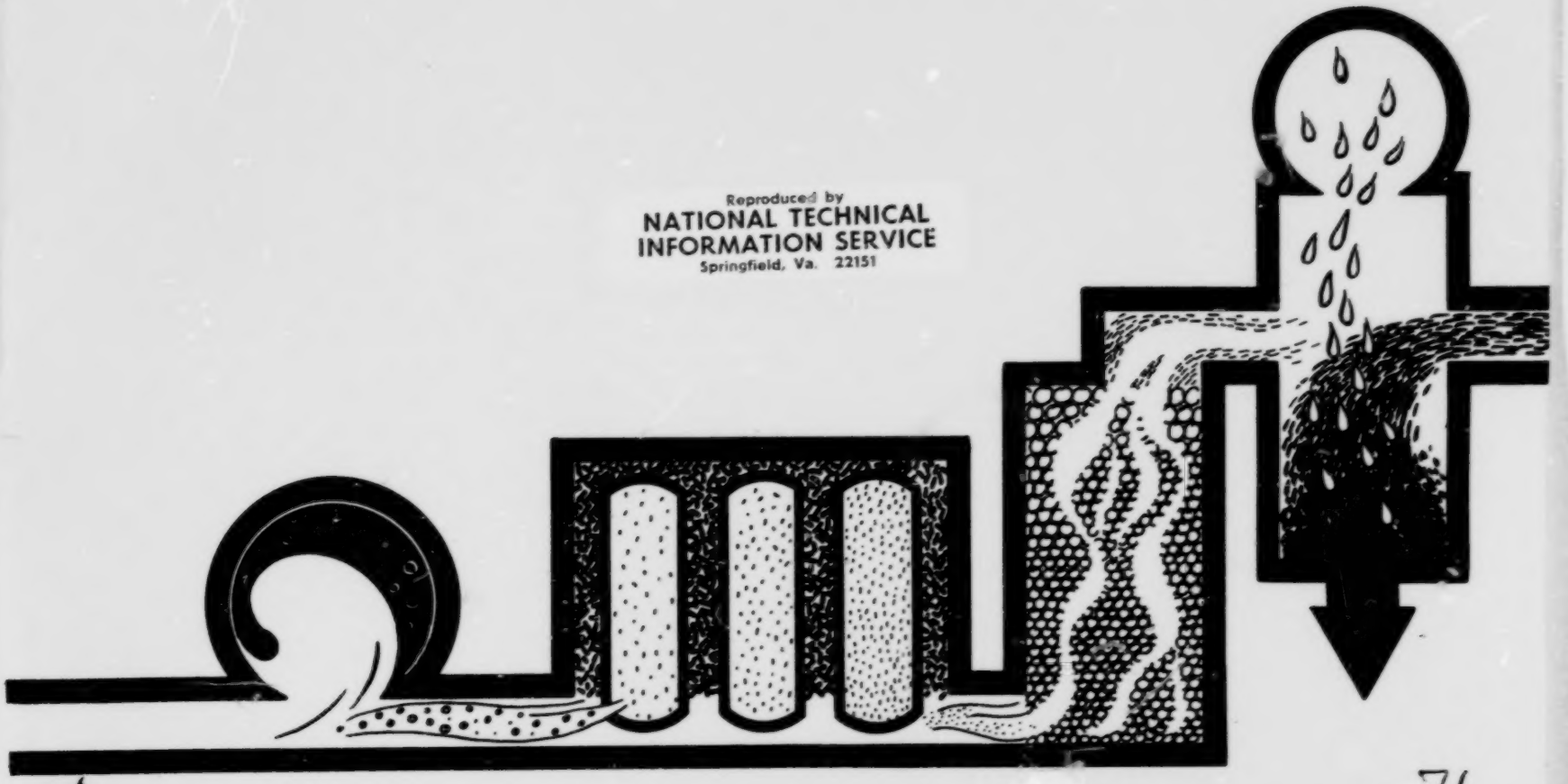

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16. Abstract Laboratory studies of a chemical denitrification process, namely copper catalyzed ferrous iron reduction of nitrate ion in basic media, demonstrated that denitrification of dilute (10 ppm NO_3-N) nitrate solutions to a mixture of innocuous gaseous products was possible. 95 to 98% of the reduced nitrate was in the form of NH_3, N_2, N_2O, NO_2 and unreacted NO_3. Optimum conditions for reaction were: (1) initial pH near 8 (mole ratio of OH^-/Fe^{3++} = 1.5); (2) mole ratio Fe^{++}/NO^-_3 =8; (3) concentration of catalyst 1-5 ppm Cu^{++} with the reaction being carried out under anaerobic conditions; (4) Fe^{++} ion derived from the sulfate; (5) NaOH used for pH adjustment; and (6) phosphate removed and carbonate content decreased. Preliminary investigation of reduction in a continuous flow system was encouraging. The by-product magnetite, was easily separated from the treated water in the absence of appreciable phosphate which inhibits its formation. Data from 280 experiments were tabulated. Cursory studies in potable water and secondary effluent indicate the presence of as yet unidentified inhibitory substances. (Lowry-Texas)

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DEVELOPMENT OF A CHEMICAL DENITRIFICATION PROCESS

by

Rocketdyne Research
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Canoga Park, California 91304

for the

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ABSTRACT

Chemical denitrification of dilute (10 ppm NO_3^--N) nitrate solutions has been achieved with high conversion of the nitrate to a mixture of innocuous gaseous products. Laboratory development studies of the denitrification process based on the copper catalyzed ferrous iron reduction of nitrate ion in basic media were conducted to determine the effects of process variables on the extent of reduction and on product distribution. In selected experiments the nitrogen mass balance was found to be 95 - 98% comprised of NH_3, N_2, N_2O, NO_2^- and unreacted NO_3^-. In the majority of experiments the gaseous-N products (N_2 + N_2O) were determined by difference, a valid method since hydroxylamine was shown not to be a major reduction product.

The effects of initial pH (or better the OH^-/Fe^{++} mole ratio), Fe^{++}/NO_3^- mole ratio, lime vs. NaOH for pH adjustment, catalyst concentration, catalyst recycle, anions introduced with the iron and copper, and other anions present in the water were studied at constant 10 ppm NO_3^--N concentration and constant 85° F temperature. Means for removal of inhibitory species such as phosphate and carbonate were evaluated. Limited studies were conducted on the uncatalyzed reduction of nitrite as an aid to elucidation of the chemical reactions involved in the overall process.

The influence of selected parameters on the reaction time was studied and the results were applied to continuous flow reactions.

Preliminary evaluation of the denitrification process was made using tap water and secondary effluent as reaction media.

This report was submitted in fulfillment of Contract No. 14-12-546, Program No. 17010 EEX, between the Federal Water Quality Administration and Rocketdyne, a Division of North American Rockwell Corporation.

Key Words: Denitrification, nitrates, reduction, ferrous ion, catalysis, potable water, wastewater

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CONCLUSIONS

1. Nitrate ion can be reduced by ferrous hydroxide under anaerobic conditions in the presence of a copper catalyst to a mixture of nitrogen and nitrous oxide with lesser amounts of nitrite ion and ammonia.

2. The yield of gaseous-N products (N_2 + N_2O) under current optimum conditions is ~70 percent with 70 percent conversion of nitrate ion. Yield of gaseous-N products from nitrite ion is about 90 percent with 90 percent conversion.

3. Current optimum conditions include an initial pH near 8 (mole ratio OH^-/Fe^{++}= 1.5) mole ratio Fe^{++}/NO_3^- = 8, and catalyst concentration 1 - 5 ppm Cu^{++} with the reaction carried out under anaerobic conditions, the Fe^{++} ion derived from the sulfate, NaOH used for pH adjustment, and the solution pretreated to remove phosphate and decrease carbonate content.

4. Lime can be substituted for sodium hydroxide for pH adjustment with only a small decrease in the conversion of nitrate ion to gaseous-N products.

5. The fraction of the sulfate precipitated with the iron hydroxides is small (10 - 15%).

6. Sulfate ion (150 ppm maximum) is necessary to effect formation of N_2 and N_2O and thereby decrease formation of ammonia.

7. Phosphate ion inhibits the reduction of both nitrate and nitrite ions but the effect can be largely eliminated by pretreatment to remove the phosphate.

8. Carbonate ion is a mild inhibitor, the effect of which can be nullified by lime pretreatment.

9. Preliminary examination of potable water and secondary effluent indicates the presence of unknown inhibitory substances, the effect of which is lessened by the iron salts used for denitrification. A given water would therefore need to be examined for inhibitory substances and appropriately treated to enable effective application of the denitrification process.

RECOMMENDATIONS

This laboratory process development program was limited largely to defining the limits of the process parameters and finding the optimum combination of these parameters to effect maximum conversion of nitrate ion to nitrogen and nitrous oxide. To a lesser extent means of accessing and overcoming the inhibitory effects of dissolved substances (i.e., phosphates, carbonates, silicates) were studied. Only in a preliminary manner were the effects of continuous flow reactors and of actual water sources investigated. It is recommended that selected nitrate-contaminated waters such as stainless steel waste pickle liquor or dyestuff manufacturing wastewater be used as the reaction medium for a bench scale continuous flow denitrification process evaluation.

The larger scale investigation of the process, which would include pretreatment to nullify inhibitory substances if required, would enable evaluation of both the technical and particularly the economic factors to be applied in an actual situation. Utilization of crude copperas (ferrous sulfate heptahydrate) as an iron(II) source and spent ferric chloride etchant or the copper cement derived therefrom as a catalyst source should be evaluated in such a program.

INTRODUCTION

The purpose of the work described in this report was to evaluate the parameters which affect both the extent of the dilute solution reduction of nitrate ion and the product distribution in the copper catalyzed reaction with ferrous iron under basic conditions. Included in the study were the mole ratio of Fe^{++}/NO_3^-, initial pH, buffering agents, role of the accompanying anions, catalyst effectiveness, and reaction time. Means of limiting the amounts of soluble materials introduced in the process and optimization of the process were investigated as well. Preliminary attempts were made to apply the process to removal of nitrate ion from both a potable water supply and municipal wastewater.

At present, the only practical method for removal of nitrate ion from dilute aqueous solution is biological denitrification such as is found in trickling filters and activated carbon columns. Ion exchange is an efficient process but its applicability is seriously limited because of the relatively high cost and fouling of the resins. A chemical treatment process for removal of nitrate ion would be most advantageous because of its flexibility and inherent reliability. To be practical, such a chemical treatment would have to convert the nitrate nitrogen into an easily removed or biologically near-inert form while introducing a minimum amount of less objectionable chemical species into the treated water. Of equal importance in making chemical treatment a practical process is that the cost be low.

The recent feasibility study (Gunderloy, 1968) conducted in the Rocketdyne laboratories for FWQA indicated that the copper catalyzed ferrous iron reduction of nitrate in dilute basic solution was potentially capable of development into both an efficient and economic chemical denitrification process. Indicated in the feasibility study were the following points: (1) complete reduction of nitrate could be achieved, (2) nearly half of the nitrogen was neither NO_3^-, NO_2^- nor NH_3 in solution (the missing-N was believed to be N_2 or N_2O), (3) under anaerobic conditions the extent of nitrate reduction and the product distribution were pH dependent, (4) the pH of the medium changed markedly during the course of reaction, (5) reduction occurred under aerobic conditions only at high pH, (6) catalyst type and concentration were important variables, (7) phosphate inhibited the reduction of nitrate, (8) carbonate altered the nitrogenous product distribution, and (9) lime could be used in the process for pH adjustment without difficulty. At the end of the feasibility study it was apparent that considerable process oriented research would be required to evaluate the potential of this denitrification process. Possible areas of application include (1) reclaiming municipal waste waters to permit storage without excessive growth of algae, (2) reclaiming industrial waste waters where co-pollutant species are toxic in biological denitrification, and (3) purifying potable water sources contaminated with nitrate and/or nitrite to eliminate diseases

associated with these ions such as methemoglobinemia in human infants or goiter and bloating in livestock.

The investigation reported herein was divided into two phases. The first and larger of the two phases was a stepwise study of the effects of each of the variables on the reaction conducted essentially as jar tests (although somewhat more sophisticated as required). In the second phase, the process was carried out in a flow system in an effort directed toward optimization of variables and to gain an insight into problems unique to the dynamic process. As a practical matter, work on the second phase was initiated before completion of the first phase. The individual tasks of Phase 1 outlined below as discreet areas of study are in many instances inter-related.

1. Identify the "missing'N" and obtain a nitrogen material balance in gaseous, liquid, and solid phases of the reaction mixture.

2. Study the effect of varying Fe^{++}/NO_3^- ratio at constant NO_3^--N concentration.

3. Compare the effect of the anions on the process when the ferrous source is either $FeSO_4$ or $FeCl_2$.

4. Study the effect of initial pH and in addition the effect of buffers.

5. Determine the distribution of sulfate and chloride between the solid and liquid phases of the reaction mixture.

6. Seek more effective and more economical catalyst and study catalyst recycle.

7. Seek means of overcoming the deleterious effects of phosphate, carbonate, or other species present in waters to be treated.

8. Determine minimum reaction time.

9. Evaluate in preliminary fashion the effects of naturally occurring (and possibly unknown) species in both potable and municipal waste waters.

EXPERIMENTAL

Reagent solutions were prepared from A.C.S. Reagent grade chemicals with helium deaerated distilled water and either used immediately or stored under 0-25 psig of helium in borosilicate glass pressure burets (Stone, 1948) fitted with Teflon needle valves. During the course of the work it became evident that the sodium hydroxide stock solution was attacking the glass container and a stainless steel and polypropylene system was substituted. A calcium hydroxide slurry was maintained in a magnetically stirred polyethylene bottle under nitrogen. The concentrations of the reagent stock solutions used in the reported study are listed in Appendix I.

A typical experiment is described below. A 200 ml volumetric flask was placed under a bell jar which was swept with a stream of helium, a portion of which was directed to the bottom of the volumetric flask. The helium was saturated with water vapor by passing it through a fritted tube in a 45-liter bottle which also served as the supply reservoir for deaerated water. Approximately 190 ml. of the deaerated water was added to the volumetric flask through a hole in the top of the bell jar where the helium stream exited. If required an aliquot of the Na_2HPO_4 stock solution (and/or other inhibitory substances) was added to the reactor from either a syringe filled under helium in a glove bag or from a pressure buret (5 ml graduated in 0.01 ml) without contact with atmospheric oxygen by inserting the syringe needle or buret tip well into the neck of the reaction vessel. The $FeSO_4$ or $FeCl_2$ and the $CuSO_4$ (or other catalyst) was added next from a pressure buret in a similar manner. At this time, a glass electrode was inserted into the helium stirred solution. An aliquot of the NaOH [or $Ca(OH)_2$] stock solution, measured into a syringe in a helium-filled glove bag, was added rapidly to the mixture. After approximately 5 minutes, the pH of the mixture was recorded as the initial value. An aliquot of the KNO_3 stock solution was added from a pressure buret and the mixture was brought to volume with additional deaerated water. A Teflon-coated magnetic stirring bar was added, the glass stopper was inserted, and the flask was placed in an 85° F constant temperature bath. The mixture was stirred magnetically for 24 hours during which time the appearance of the suspended solids typically changed from flocculant blue-green through gray-green to a readily settleable black magnetic powder. After replacing the reaction vessel under the helium-swept bell jar, the stopper was removed and the final pH was determined. The mixture was transferred to a 200 ml screw cap centrifuge bottle under helium and centrifuged for ca. 5 min. at 1725 rpm. The supernatant solution was analyzed immediately for nitrate, nitrite, ammonia, and whatever other constituents of interest that might be present as indicated in the section on analytical support.

In some experiments (as noted) the order of addition of the reagents was varied to determine any effects on the reaction. In the typical

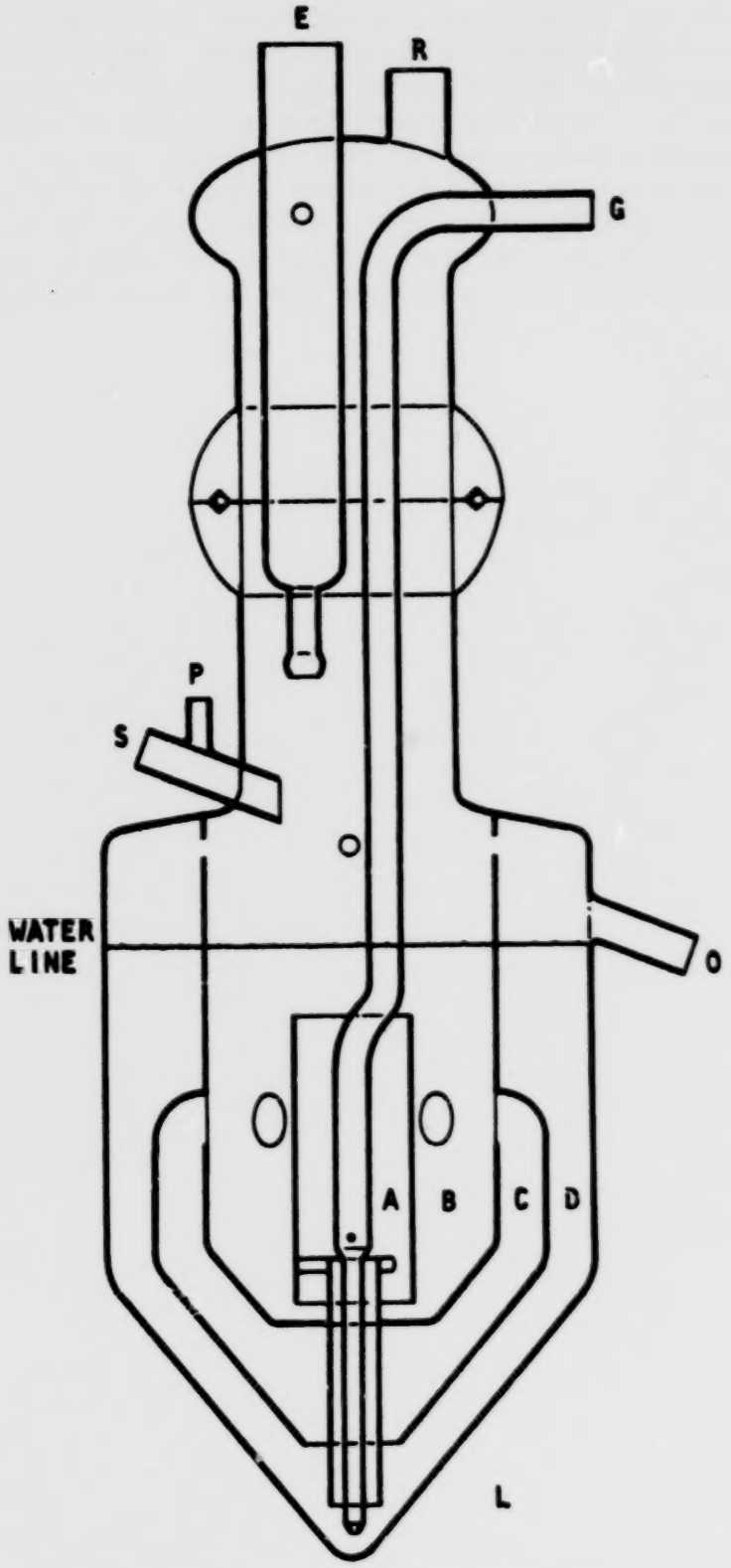
experiment as described above the nitrate solution was added last because under these conditions a more stable initial pH value could be obtained.

Certain experiments were carried out in the typical manner using larger volumes of solution to permit multiple sampling for analyses at varying reaction times. Under these circumstances a helium stream was directed into the mixture during sampling to prevent entry of air. In other experiments wherein continuous addition of reagents from a syringe pump was used, a continuous sweep of water-saturated helium was used to maintain anaerobic conditions.

The experiments concerned with collection and mass spectrometric analysis of the gaseous-N compounds required only a slight modification of the closure for the reaction vessel. The conventional glass stopper was replaced by another which extended into the neck of the flask to minimize the ullage and which was equipped with a Teflon needle valve to permit removal of the contents directly into a vacuum line. The ullage volume 2.53 cc was determined from the weight difference between the completely water-filled apparatus and the apparatus filled to the 200 ml calibration mark. An initial attempt was made to degas the solution by boiling off the dissolved gases into the vacuum line and collecting the material passing a -143 C trap for mass spectrometric analysis (Expts. 16, 18 and 25). This procedure was too lengthy and accordingly was modified by inverting the reactor and discharging the entire reaction mixture into an evacuated 1000 ml receiver where degassing was effected rapidly by the freeze-thaw technique.

In the continuous flow experiments with solids retention (see Fig. 1), anaerobic conditions were maintained by the helium stream introduced through G to stir the reaction mixture. The effluent helium from P was lead over the gas intakes of the variable flowrate constant head siphons used to supply reagent solutions which were introduced through the rubber septum S by means of 3" #22 needles. In the series of annular chambers rapid mixing was attained in A (upflow) and B (downflow) with moderate agitation in C (downflow) with an upflow return to A from the bottom of the reactor. Chamber D was an unstirred upflow clarifier which accounted for 230 ml of the total 465 ml reactor volume. The effluent flowed from O to a sample collecting reservoir outside the constant temperature bath L in which the reactor was immersed. The pH was measured with a glass electrode introduced through E. The port R was used to introduce a small (0.1 ml) cup in which the ferrous and cupric hydroxides were coprecipitated before falling into the stirred chambers A and B.

The second design for a continuous flow reaction was simply an 8 mm I.D. tube with a 15 cm section (7.5 ml) with inlets for introduction of ferrous and cupric sulfates and sodium hydroxide near one end and a pH electrode followed by an inlet for potassium nitrate at the other just preceding a 121 cm thermostatted reaction section (60.5 ml). The reactor was stirred by a stainless steel spiral (2 cm pitch) countercurrent to



CROSS SECTION OF FLOW REACTOR

FIGURE 1

the liquid flow at a speed just sufficient to suspend the precipitate. The reagent inlets as well as the effluent in a sample collecting reservoir were maintained in a helium atmosphere. The $FeSO_4$ and NaOH solutions were introduced with syringe pumps into the $CuSO_4$ solution (ca. 20% of total flow) which was delivered from a variable flowrate constant head siphon. After pH measurement of the preformed mixing hydroxides suspension, the KNO_3 solution was introduced from a similar siphon. A periodicity in the pH indicated that the flowrates used (17 ml/hr. for $CuSO_4$) were too low to obtain constant flow from the siphon as a result of the periodic introduction of the helium bubbles into the siphon reservoir.

DISCUSSION

In the discussion below of the effects of each of a number of variables on the extent of reduction of nitrate ion and the resulting nitrogenous product distribution, the pertinent experiments are grouped together. The experimental detail for each experiment will be found in the appropriate appendix. As the discussion is arranged the experiments are not necessarily in chronological order but this order may be deduced from the numerical order of the experiments. In many cases, an experiment will appear in more than one appendix for convenience in making comparisons if the data are pertinent to more than one of the variable parameters.

In all of the experimental work a constant temperature of 85° F was used first, because this appeared to be a realistic upper limit for waters in which this denitrification process might find application, and, second, because more rapid reaction at this upper temperature limit would expedite the investigation of the numerous variables.

IDENTIFICATION OF THE GASEOUS-N SPECIES

In the earlier feasibility study (Gunderloy, 1968) an unsuccessful attempt was made to identify the "missing-N" by mass spectrometric analysis of the gaseous nitrogen products as a part of obtaining an overall nitrogen material balance. In that experiment the wet analyses for nitrate, nitrite and ammonia accounted for 96.4% of the nitrogen effectively precluding the mass spectrometric data. Additional experiments reported herein have established that the conditions used were far from optimum for reproducible formation of gaseous-N compounds. In the successful experiments (tabulated in Appendix II) the initial pH was lower (7.8 - 8.4 vs. 11) than was used in the early work. In the final duplicate experiments 64 and 59% of the NO_3^--N was converted to a mixture of N_2O and N_2 (N_2O/N_2 = 1.46) with an overall material balance of 95 and 98%, respectively. In numerous subsequent experiments the yield of the gaseous-N (determined by difference) was increased but these experiments were not set up to collect and analyze the gaseous-N compounds; it is not known how the ratio N_2O/N_2 varies within the limits of our experimental conditions or whether it is invariant.

The identification of N_2O as a product of the denitrification process poses the question of air pollution if large quantities of this nitrogen oxide were generated. The two primary photochemically induced decomposition reactions of N_2O are

$$N_2O \rightarrow N_2 + O \qquad (1)$$

and

$$N_2O \rightarrow NO + N \qquad (2)$$

of which the first accounts for 88% (McNesby, 1964). Secondary reactions such as

$$N + O_2 \rightarrow NO + O \qquad (3)$$

and

$$NO + O_2 \rightarrow NO_2 + O \qquad (4)$$

would form some pollutants but the concentration would probably be too small to cause concern (Bates, 1967).

THE EFFECT OF INITIAL pH

The initial pH of the reaction mixture would be expected to influence strongly the denitrification reaction since the reducing power of ferrous iron increases as the ratio of Fe^{+++}/Fe^{++} decreases. As a result of the relative solubilities of $Fe(OH)_3$ and $Fe(OH)_2$ ferrous ion becomes a more powerful reducing agent as pH increases. Complete reduction of nitrate to ammonia without catalysis has been demonstrated in 28% sodium hydroxide solution (Carsley, 1930) but proceeds only to the extent of 1-3% in 3% sodium hydroxide unless catalysts such as silver or copper are used (Szabo, 1951).

In the feasibility study (Gunderloy, 1968) the copper catalyzed reduction of nitrate ion in dilute solution was shown not to proceed at initial pH $\leq$ 6. With increasing pH the extent of reaction increased to near quantitative but products other than ammonia were observed. The data were not without anomalies, however, prompting the reinvestigation of the effect of pH reported herein.

At the time that most of the experimental data were being obtained, the fact that OH^-/Fe^{++} mole ratio would be a better experimental parameter than pH was not fully appreciated. The flatness of the potentiometric titration curve for $FeSO_4$ or $FeCl_2$ causes pH to be a rather insensitive parameter within the range of 0.25 - 1.75 for the OH^-/Fe^{++} mole ratio. At low mole ratios the lack of buffering capacity resulting from the limited amount of $Fe(OH)_2$ permitted the pH to fall to a low value where the reducing power of the ferrous iron decreased rapidly. As a result both NO_3^- and Fe^{++} remained unused in many experiments. Conversely, at high mole ratios the buffering capacity of the $Fe(OH)_2$ maintains the pH at a value favoring complete reduction to ammonia.

The pertinent experiments summarized in Appendix III all were run at 10 ppm NO_3^--N with a Fe^{++}/NO_3^- mole ratio of 8, a OH^-/Fe^{++} mole ratio of 1.45 - 1.46, and 5 ppm Cu^{++} catalyst with both metal ions derived from the respective sulfates. If the data from experiments 1 - 4 are not included (initial pH values not reliable due to variable rates of introducing the NaOH solution to the nitrate-containing solution), a decreasing

trend in the extent of nitrate ion reduction with decreasing initial pH is clearly evident. After 24 hours at pH 11, no nitrate remained, only about 1% of the original amount at pH 8.7, 7% at pH 8.0, and 39% at pH 7.4. Particularly significant is experiment 273 which was analyzed periodically during the 24-hour reaction period. Comparison of the sample pH and the analytical data (See Appendix XXI) indicates that the rate of conversion of nitrate to nitrite drops off sharply in the pH range 7.0 - 7.3. The drop in pH noted during the first hour of reaction was reversed during the second hour was presumably due to formation of nitrite (basic in solution) which would overcome the acidifying effect of the oxidizing iron (Equation 5).

$$Fe(OH)_2 + H_2O \rightarrow Fe(OH)_3 + H^+ + e^- \qquad (5)$$

Further reduction of the nitrite would result in the observed drop in pH and formation of gaseous-N compounds. This rationale appears somewhat less plausible when the reduction of nitrite is considered since the same pH-time relationship was observed (see Reduction of Nitrite). Although the experimental data offer no definitive proof, they are consistent with the postulated formation of ferrous hyponitrite, an unstable compound reported to form at pH 6.5 - 7.0 and to decompose immediately with evolution of an unknown gas (Polydoropoulos, 1961).

With respect to the effect of pH on the yield of ammonia the experiments summarized in Appendix III clearly show the trend to decreased yield with decreasing pH but other factors not indicated definitively by these data effect the yield as well. These factors are (1) the aforementioned OH^-/Fe^{++} mole ratio which, if too high, maintains a pH favoring ammonia formation, and (2) catalyst aging which will be discussed later also favors formation of ammonia. In the uncatalyzed reduction of nitrite, ammonia is the exclusive product at high initial OH^-/Fe^{++} mole ratio (e.g., 1.82, see Reduction of Nitrite).

EFFECT OF THE BASE - NaOH VERSUS $Ca(OH)_2$

In the majority of the experiments sodium hydroxide was used to adjust the pH of the reaction mixture simply because of the ease of introducing a solution compared to that of a slurry or a solid as is required with calcium hydroxide. However, in one series of experiments a direct comparison of the effect of substituting a 1% $Ca(OH)_2$ slurry for 0.98 M NaOH was evaluated. The data tabulated in Appendix IV indicate that the conversion of nitrate to reduced species was approximately 15% less with $Ca(OH)_2$ than with NaOH but the yield of gaseous-N compounds was identical within the experimental error. Thus, it appears that the presence of calcium ion inhibits the nitrate to nitrite reduction step only.

EFFECT OF Fe^{++}/NO_3^- MOLE RATIO

The reduction products observed in the denitrification process, NO_2^-, N_2O, N_2 and NH_3, theoretically require 2, 4, 5 and 8 moles of Fe^{++} per

mole of NO_3^-. However, the pH range in which the reduction reactions occur to give these products falls within the range favoring formation of ferrous ferrite (magnetite), Fe_3O_4, namely from pH 6.2 - 11.4 (Krause, 1955). Thus, the theoretical Fe^{++}/NO_3^- ratios are 3, 6, 7.5 and 12, respectively. It is immediately apparent that in order to minimize the amount of soluble counterions ($SO_4^=$ or Cl^-) introduced into the receiving waters the minimum amount of ferrous salt should be used in the denitrification process.

Considering first the information derived from experiments using sulfate only as the counterion (Appendix V), the conversion of NO_3^- to gaseous-N appears not to change greatly from Fe^{++}/NO_3^- ratios from 12 to 5 (60 ± 5%) and then decreases as the ratio drops to 2. The yields of gaseous-N compounds imply only a slight downward trend over the Fe^{++}/NO_3^- ratio range 12 to 4 becoming more apparent as the ratio drops to 2. This constancy in the yield of gaseous-N compounds over the wide range of Fe^{++}/NO_3^- ratios is interpreted to mean that the formation of gaseous-N compounds is independent of the amount of ferrous iron used. From an inspection of the data in Appendix V, it is evident that at high OH^-/Fe^{++} mole ratios with sufficient ferrous iron ammonia is the major product with concomitant decrease in gaseous-N products.

When ferrous chloride was used as the source of the reducing agent (see Appendix VI), ammonia appears as the major product even though the ratio OH^-/Fe^{++} was no greater than 1.54. As a function of the Fe^{++}/NO_3^- ratio no trend is evident in the amount of NO_3^- converted to gaseous-N products. Although the yield of gaseous-N products appears to increase with decreasing Fe^{++}/NO_3^- ratio, the simultaneous decrease of the OH^-/Fe^{++} ratio might better account for this observation. The seemingly anomalous results among the experiments at a Fe^{++}/NO_3^- ratio of 8 is a result of the use of $CuSO_4$ catalyst in lieu of $CuCl_2$ and, accordingly, will be discussed in the section concerned with the effects of anions on the denitrification process.

CATALYST EVALUATION

The reduction of nitrate with ferrous hydroxide has been studied quite extensively as an analytical method and as such the experimental conditions were selected to give quantitative reduction to ammonia. The catalysts most commonly used are copper and silver salts both of which were used in the feasibility study (Gunderloy, 1968). Silver salts were not further considered in the present study for economic reasons.

The effect of the copper catalyst concentration was studied in more detail than in the initial study (Gunderloy, 1968) wherein the concentrations, 1, 5 and 10 ppm Cu^{++} were evaluated only at pH 11, a value far too high for significant formation of gaseous-N compounds. Copper concentrations from 0.05 ppm (resulting from a copper impurity in the reagent ferrous sulfate) up to 5 ppm were evaluated at a ratio OH^-/Fe^{++} = 1.46

(pH near 8.3). The data, listed in Appendix VII, indicate that nitrate reduction occurred effectively at copper concentrations as low as 1 ppm. The product distribution appeared not to change with copper concentration in the range of 1 - 5 ppm where 65 - 75% of the initial NO_3^--N was converted to gaseous-N compounds and about 20% to ammonia.

The effect of the order of addition of the catalyst with respect to the other reagents was studied briefly (Appendix VIII). With all other conditions held constant in 24-hour experiments, the effect on product distribution of coprecipitation of the copper and iron hydroxides as opposed to addition of the cupric salt to the precipitated ferrous hydroxide was evaluated. A somewhat greater reduction of nitrate was observed with the coprecipitated hydroxides--91% vs. 81%. Individual differences in the values of nitrite and gaseous-N products are not significant but presumably reflect only the lowering of pH to a value where reduction stopped. It may be noted that the summation of the nitrite and gaseous-N is constant for each set of experimental conditions, i.e., ca. 67% of the original nitrogen with coprecipitated hydroxides and ca. 52% with catalyst added last. The amount of ammonia produced was nearly the same after 24 hours for either set of experimental conditions but with normal addition of catalyst it was formed during the first hour.

Because of the obvious economic advantage the possibility of recycling the catalyst was investigated. The absence of copper in the solution after reaction indicated that all of the catalyst had coprecipitated with the black magnetic Fe_3O_4. The first attempt at recycling the catalyst was simply to add the black solids from a prior reaction to another reaction mixture in lieu of the copper salt. The extent of nitrate reduction was a little less but roughly comparable to that observed in the reaction using fresh catalyst. However, the amount of ammonia formed was approximately twice the usual quantity with a corresponding decrease in the amount of gaseous-N compounds formed. Confirmation of this observed increase in the yield of ammonia in the presence of the copper-containing Fe_3O_4 was obtained in a flow reaction (to be discussed in more detail in another section). The data are tabulated in Appendix IX. Included in Appendix IX is data from an experiment where the cupric hydroxide had been coprecipitated with ferric hydroxide and heated at the boiling point for 24 hours in an attempt to form cupric ferrite (Forestier, 1939; Longuet, 1941). Apparently, under the conditions of high dilution used, the black ferromagnetic $Cu(FeO_2)_2$ did not form and the cupric hydroxide dehydrated to the oxide (Sidgwick, 1950). This accelerated aging of the catalyst resulted in lowered reduction of nitrate and a high yield of ammonia.

Since the aged catalyst in the Fe_3O_4 promoted formation of ammonia the feasibility of extracting the copper from the solid was investigated briefly. The acidic ferrous sulfate reagent solution was used at 100-fold dilution to leach the precipitate under anaerobic conditions. The concentration of copper in solution was determined periodically and

indicated that approximately 40% of the copper is recovered within 0.25 hour and over 80% in 24 hours (Appendix X). Although not definitively established experimentally the variability of the copper concentration may result from competition of reactions which decrease (equations 6 and 7) and increase (equation 8) the soluble cupric ion. The last reaction

$$Cu^{++} + Fe^{++} \rightarrow Cu^{+} + Fe^{+++} \qquad (6)$$

$$2Cu^{+} \rightarrow Cu^{++} + \underline{Cu} \qquad (7)$$

$$2Cu + 4H^{+} + O_2 \rightarrow 2Cu^{++} + H_2O \qquad (8)$$

would be expected if air leaked into the system.

A series of experiments was conducted using elemental copper as the catalyst source (presumably the surface oxide is the actual source). Two forms of the metal, No. 1 shot and 150 mesh powder, were used to evaluate the effect of surface area. The surface area of the powder was about 68 times that of the shot. In some experiments the copper was contacted with the ferrous sulfate for an hour before addition of the base and nitrate while in others all the reagents were added in rapid sequence. The data, summarized in Appendix XI, show that the reduction of nitrate was poor in the presence of shot but very good with the powder. Visual observations of the color of the precipitated hydroxides as a measure of catalyst concentration correlate well with extent of nitrate reduction; the color with shot was almost white and with powder a pale to dark green. In addition, the color of the precipitate in all the experiments darkened with time, but only in those using powder did the black Fe_3O_4 form. In the experiments using powder the high conversion of nitrate to ammonia (47%) and to nitrite (50%) is not surprising at the high OH^{-}/Fe^{++} ratio used (ca. 1.85, cf. data in Appendix III).

A still more economical source of copper than scrap metal is the copper-cement recovered during regeneration of ferric chloride copper etchants. The cement and spent etchant solution were analyzed for copper and iron content but were not evaluated in denitrification experiments because the samples were received just prior to the termination of the experimental work. The spent etchant analyzed 3.7% copper and 10.2% iron while the cement (after mechanical separation from 0.63 of its weight of tramp iron) analyzed 27.4% copper and 21.6% iron.

Only a preliminary effort was made to evaluate other metals as catalysts. The potential catalyst must be capable of entering into redox reactions and should be less expensive than copper. These criteria limit the potential candidates severely so that only lead was evaluated. Lead has been reported to catalyze the oxidation of ferrous hydroxide by oxygen (Krause, 1937) beyond the ferrous ferrite stage. Although the cost of lead is only about one-fourth that of copper the greater atomic weight

offsets most of the economic advantage of lead. Under the conditions chosen for the preliminary experiments the reduction of nitrate was poor and the principal product was ammonia (see Appendix VII) so that evaluation was not pursued further.

EFFECTS OF ANIONS

Since the denitrification process is the reduction of nitrate ion by ferrous hydroxide, it may be assumed initially that only hydroxide ion exerts an important effect on the course of the reaction. That this assumption is naive was shown by a comparative study of the two economical sources of ferrous ion, ferrous sulfate and ferrous chloride. The major experimental effort was carried out using ferrous sulfate, which currently in many locations is a surplus commodity requiring disposal. Dumping at sea is being used where feasible as a more economic means of disposal than recovery of the sulfuric acid and iron oxide values by existing technology. The simpler recovery of hydrochloric acid and iron oxide values from ferrous chloride will doubtless mean that this salt will not be as cheap a source of ferrous ion as the sulfate. However, the rapidly growing importance of hydrochloric acid for pickling of steel (Anonymous, 1969) dictated that ferrous chloride should be evaluated as well. In addition to the counter ions introduced with the iron and copper salts, the effects of other anions commonly found in waters requiring denitrification, such as phosphate, carbonate and silicate, were evaluated. In all cases the system containing only sulfate in addition to hydroxide and nitrate (and its reduction products) is used as the basis for comparison of the effects of other anions.

The mechanism by which the various anions influence the reaction rates and/or the distribution of reduction products of the nitrate ion would be of considerable importance to the understanding of the denitrification process. To be considered is the ability of the anion (1) to buffer the reaction medium, (2) to precipitate or complex either the catalyst or the reducing agent or both, and (3) to alter the electrical surface charge of the precipitated iron and copper compounds. Available experimental data bearing on these considerations will be discussed within the study of the effects of the individual anions.

Comparison of Chloride and Sulfate

An inspection of Appendices V and VI reveals that a direct comparison of the effects of chloride vs. sulfate on the distribution of reduction products is not possible because of differences in the OH^-/Fe^{++} ratio at a given Fe^{++}/NO_3^- ratio. However, where differences in the OH^-/Fe^{++} ratio at a given Fe^{++}/NO_3^- ratio are not too great a valid comparison of the effects of the individual anions can be made. For example, where $Fe^{++}/NO_3^- = 8$ and $1.46 < OH^-/Fe^{++} < 1.54$ using NaOH for pH adjustment, the yield of gaseous-N products was decreased from 77% (with 94% NO_3^- reduction) in the sulfate system to 3% (with 56% NO_3^- reduction) in the

chloride system. The same effects were noted at Fe^{++}/NO_3^- = 5 where OH^-/Fe^{++} = 1.72 in the sulfate system and OH^-/Fe^{++} = 1.51 in the chloride system, i.e., gaseous-N yield 62% (with 87% NO_3^- reduction--sulfate) and 31% (with 36% NO_3^- reduction--chloride). With ferrous chloride the apparent increase in yield of gaseous-N products as Fe^{++}/NO_3^- decreases can be better explained as the result of the decrease in OH^-/Fe^{++} ratio. In contrast in the ferrous sulfate experiments where OH^-/Fe^{++} was held constant as Fe^{++}/NO_3^- decreased, the yield of gaseous-N products falls off significantly near Fe^{++}/NO_3^- = 3. Therefore, it appears that at any given ratio of Fe/NO_3^- and OH^-/Fe^{++} a greater yield of gaseous-N products will be obtained using ferrous sulfate rather than ferrous chloride.

In a series of experiments at constant Fe^{++}/NO_3^- = 8 and OH^-/Fe^{++} = 1.45 (Appendix IV) where a variable mixture of ferrous sulfate and chloride was used with a copper sulfate catalyst, the yield of gaseous-N products drops only 10% on replacing three-fourths of the ferrous sulfate with ferrous chloride. The dramatic effect of sulfate on the yield of gaseous-N products is evident from the experiments where only 7.6 ppm $SO_4^=$ (from the $CuSO_4$ catalyst) increased the amount of gaseous-N by an order of magnitude over the sulfate-free system (45% vs. 4%). Thus, a relatively small concentration of sulfate (ca. 100 - 150 ppm) is all that is required to permit the denitrification process to proceed satisfactorily in waters of high chloride concentration.

The amount of sulfate precipitated by the basic iron compounds decreased from 5 - 10% to less than 3% as the OH^-/Fe^{++} ratio increased from 1.46 to 1.89 when all of the iron was supplied as sulfate and pH was adjusted with NaOH (Appendix III). When only one-fourth of the iron was supplied as sulfate and the remainder as chloride, 13% of the initial sulfate precipitated with the black iron compounds. In contrast, the amount of chloride which precipitated with the iron compounds increased rather than decreased with increasing anion concentration but the maximum was only about 5%. These maxima were increased when calcium hydroxide was substituted for sodium hydroxide for pH adjustment but only to 19% for the sulfate and 6% for the chloride precipitation.

A possible means of limiting the amount of anions introduced into the treated water has been reported (Gotz, 1963). The cyclic process which utilizes concentrated (6 - 10%) solutions is based on the equations (9) and (10). The separated gypsum may be disposed of as solid waste (or

$$FeSO_4 + CaCl_2 \rightarrow CaSO_4 + FeCl_2 \qquad (9)$$

$$FeCl_2 + Ca(OH)_2 \rightarrow Fe(OH)_2 + CaCl_2 \qquad (10)$$

sold) while the separated $Fe(OH)_2$ is used in the denitrification process. Sufficient sulfate would accompany the $Fe(OH)_2$ to permit efficient denitrification.

In keeping with the greater solubility of the basic iron chloride as compared with the sulfate at a given pH, potentiometric titration of ferrous sulfate shows that in the presence of chloride ion the precipitation of hydroxide occurs at a higher pH (Levin, 1956). Potentiometric titrations of dilute solutions of ferrous sulfate and ferrous chloride gave almost superimposable curves (Figure 2) except that initial precipitation of the hydroxide occurred at a lower pH in the sulfate system. The addition of 5 ppm Cu^{++} accentuated initial precipitation at lower pH in the sulfate system more so than in the chloride system (Figures 2 and 3) as a result of the oxidation of some of the iron to the ferric state (Arden, 1950). It is postulated that the lower pH of the basic sulfate as compared with the basic chloride allows intermediate formation of ferrous hyponitrite (Polydoropoulos, 1961) in this system while intermediate hydroxylamine is formed at the higher pH in the chloride system. Presumably both of these compounds arise from a common intermediate, nitroxyl (Brown, 1967), and then further react to give the principal observed products, N_2 and N_2O from FeN_2O_2 decomposition and NH_3 from NH_2OH reduction.

Effect of Phosphate

In the feasibility study (Gunderloy, 1968) the value of the experiments concerned with the effect of phosphate on the denitrification process was limited since a number of variables were changed simultaneously. These experiments did serve to show (1) that phosphate had a strong inhibitory effect on denitrification, and (2) that the inhibitory effect could be overcome either by increasing the Fe^{++}/NO_3^- ratio or substituting silver for the copper catalyst. It is now known that the experimental conditions used were such that little, if any, formation of nitrogen or nitrous oxide would be expected.

A number of experiments were run at selected phosphate concentrations and varying pH to delineate the extent of the inhibition and the influence that phosphate might have on product distribution. If the series of experiments at a constant 2 ppm $PO_4^{\equiv}$-P is considered first (Experiments 229 - 238, Appendix XIII), it is apparent that over the pH range 7.3 - 9.5 the reduction of nitrate is significantly decreased. The extent of reduction was only about 10% at the lower pH (OH^-/Fe^{++}= 0.63) and 28% at the upper pH (OH^-/Fe^{++}= 1.80) with a maximum of 38% reduction at an intermediate pH of 7.7 (OH^-/Fe^{++}= 1.63). The principal reduction products at $OH^-/Fe^{++} \leq$ 1.29 were comparable amounts of gaseous-N compounds and ammonia while as the OH^-/Fe^{++} ratio rose about 1.63 nitrite ion appeared in increasingly greater proportion with a lesser amount of ammonia. In the experiments where phosphate concentration was varied at a relatively constant pH = 8.0 - 8.3, a decrease in the amount nitrate ion reduced was noted as $PO_4^{\equiv}$-P concentration increased from 0.5 to 10 ppm.

The inhibition of the denitrification process might be caused either by (1) precipitation or complexing of either the copper catalyst or the ferrous reducing agent, or (2) superposition of the phosphate buffer on

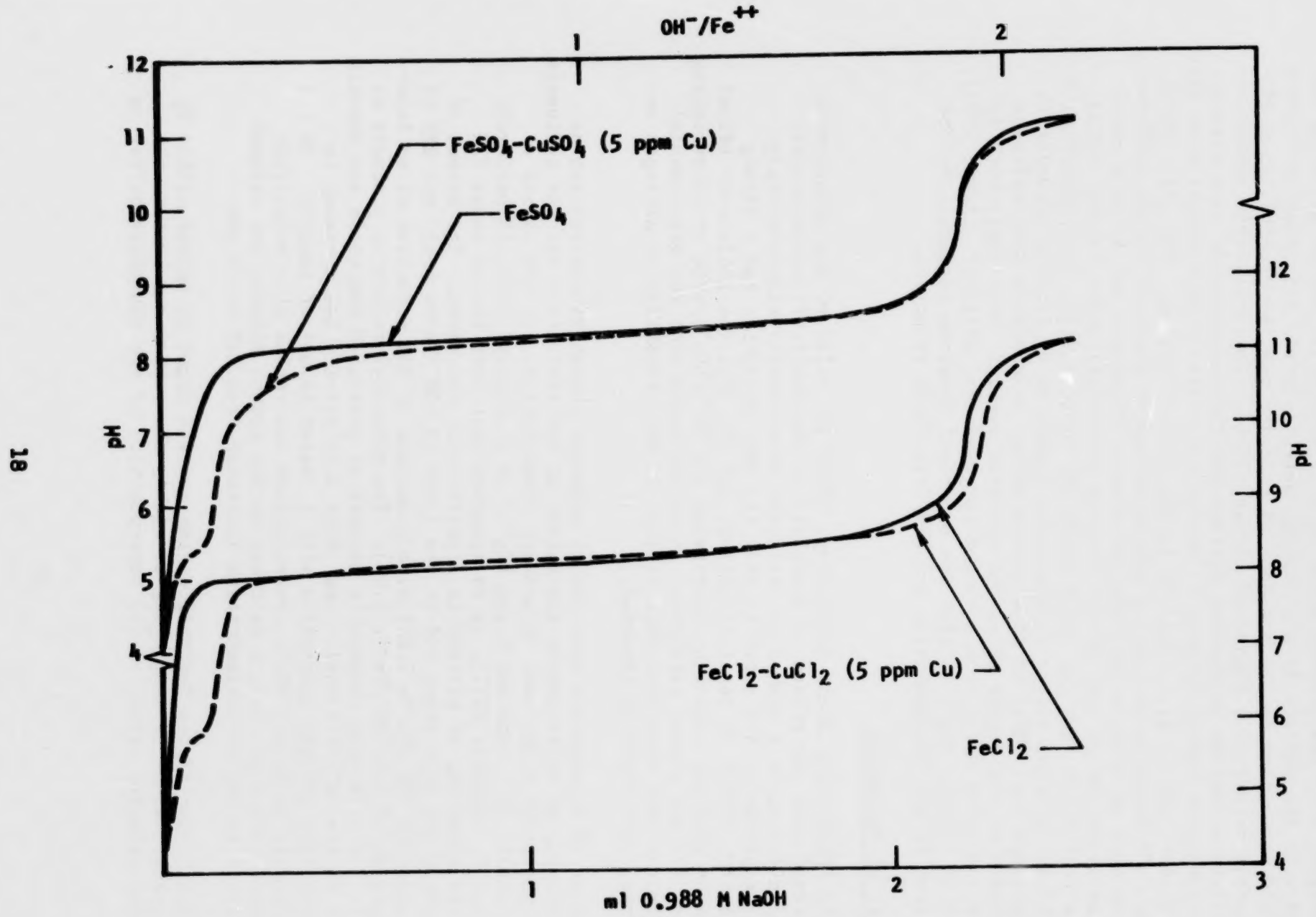


FIGURE 2. Potentiometric Titration Curves for $FeSO_4$, $FeSO_4$-$CuSO_4$, $FeCl_2$, and $FeCl_2$- $CuCl_2$

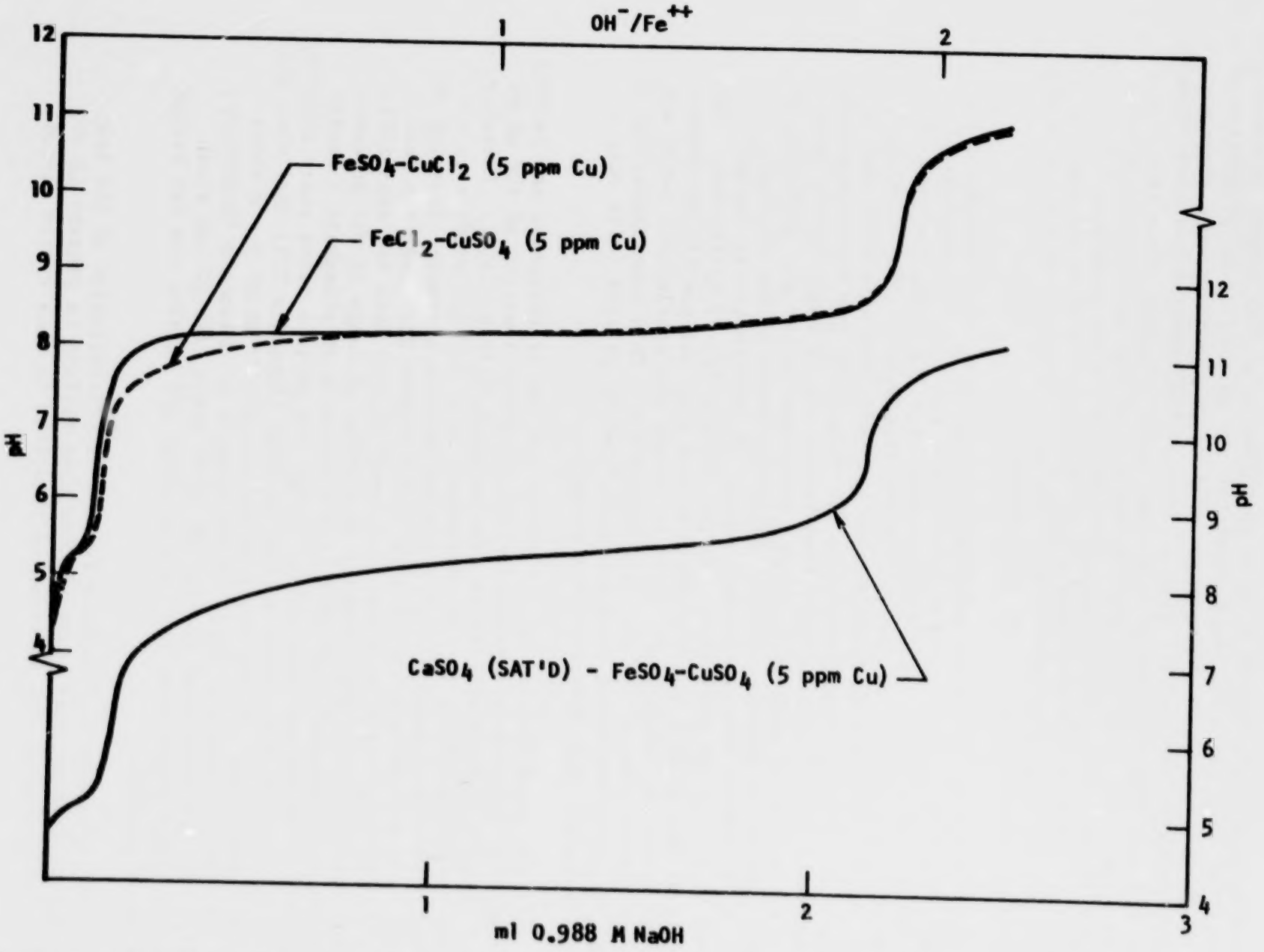


Figure 3. Potentiometric Titration Curves for $FeSO_4$-$CuCl_2$, $FeCl_2$-$CuSO_4$, and $FeSO_4$-$CuSO_4$-$CaSO_4$

the ferrous hydroxide buffer to give an unfavorable pH. Little reliable quantitative data is to be found on either the solubility of phosphates of each of the valence states of copper and iron or the complexing strength of phosphate with these metal ions. If under the experimental conditions of the denitrification process it is the copper catalyst alone which is rendered inactive, then the reduction of nitrite ion which requires no catalyst (Brown, 1967) should proceed unchanged in the presence of phosphate. That it did not (vide infra, Reduction of Nitrite) implied that either an iron-phosphate interaction or a buffering effect (or both) were mainly responsible for the inhibition.

The decolorization of ferric solutions by complexing with phosphate ion is well known in analytical chemistry. Data relating to phosphate complexing with ferrous ion is more obscure but the known decrease in the oxidation potential of the Fe^{++}-Fe^{+++} (Van Wazer, 1958) is clear-cut evidence that ferrous ion activity is diminished more than that of ferric ion. Further data bearing on the relatively greater interaction of phosphate with ferrous rather than ferric ion is found in the phosphate inhibition of magnetite, Fe_3O_4, formation in the air oxidation of ferrous hydroxide (Krause, 1963). Magnetite forms in the pH range 6.2 - 11.4 between the isoelectric points of the negatively charged ferric (5.4) and the positively charged ferrous (11.5) hydroxides. Complexing of the multivalent phosphate anions with the positively charged ferrous hydroxide would be expected to change the isoelectric point and prevent interaction of the two iron hydroxides. This same inhibition of Fe_3O_4 formation was found in the denitrification process (with only a few exceptions) when phosphate was present.

The possible superposition of the buffer actions of phosphate and ferrous hydroxide is apparently overshadowed by a drastic lowering of the pH at which the hydroxide precipitates from solution (Levin, 1956). Potentiometric titration curves at low concentration of ferrous sulfate in the presence of copper catalyst and phosphate exhibit a greater lowering of the pH than did sulfate (cf. Figure 4 with Figure 2). The fact that only partial reduction of nitrate occurred implies that the denitrification reaction proceeded normally in a given pH range in the presence or absence of phosphate but that in the presence of phosphate a lesser amount of reaction was required to change the pH to a value where reaction stopped. It should be noted on the one hand (Appendix XII) that when the OH^-/Fe^{++} ratio was low the final pH had dropped to about 5 - 6 where denitrification does not occur in the absence of phosphate (Gunderloy, 1968). On the other hand at high OH^-/Fe^{++} ratio, the pH had risen significantly higher than the initial value and nitrite ion had become the major product.

Since the presence of phosphate results in precipitation of the basic ferrous salt at an even lower pH than when sulfate is present in the $FeCl_2$-$CuCl_2$ system, the addition of phosphate to this system should

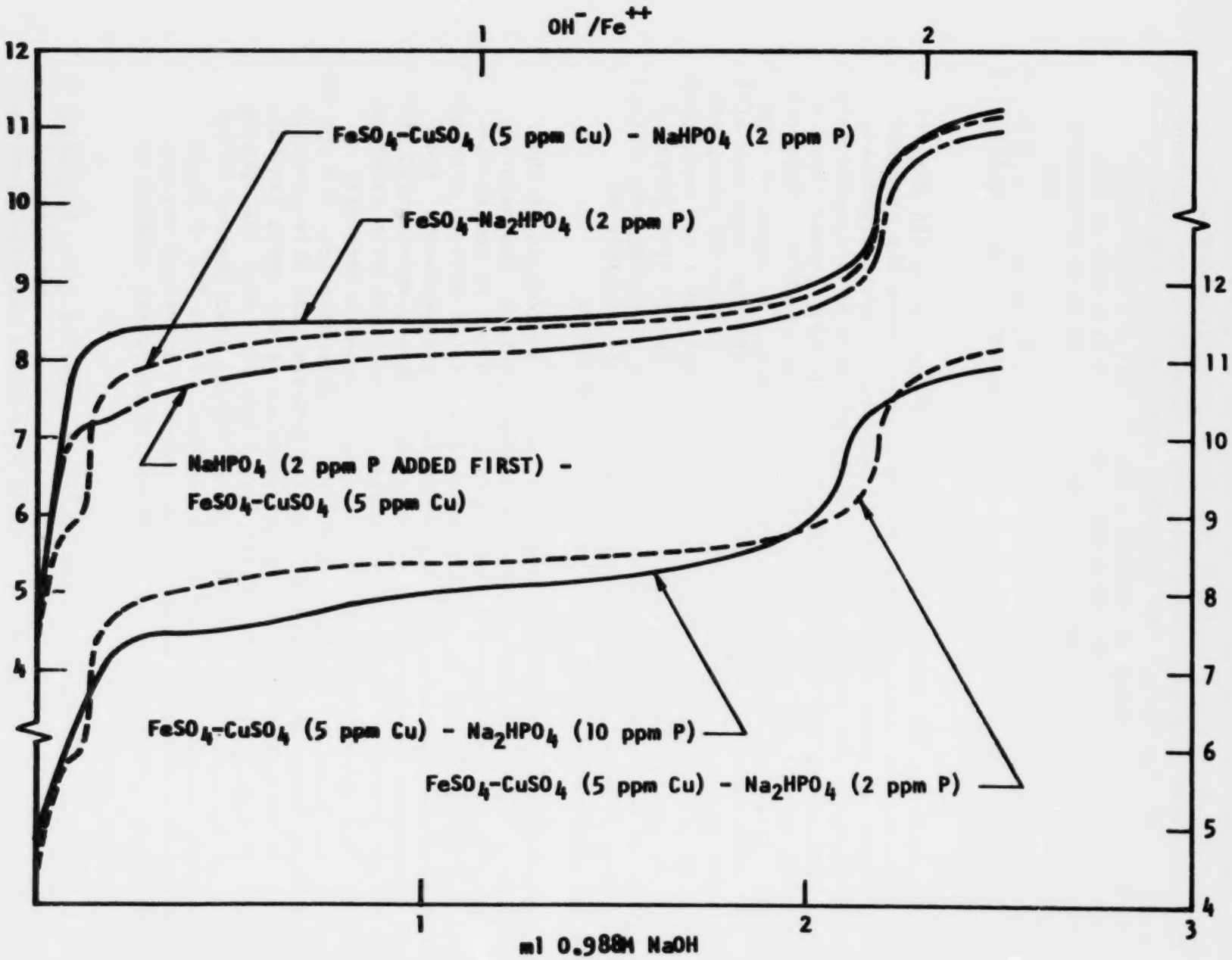


Figure 4. Potentiometric Titration Curves for $FeSO_4$-Na_2HPO_4, $FeSO_4$-$CuSO_4$-Na_2HPO_4

result in an increased yield of gaseous-N products. This postulate was verified experimentally in two series of experiments at different initial OH^-/Fe^{++} ratios and variable phosphate concentrations up to 5 ppm $PO_4^{\equiv}$-P (Appendix XIII). With increasing phosphate concentration in both series of experiments the following observations were made: (1) a decrease in the amount of nitrate reduced, (2) a simultaneous increase in yield of gaseous-N compounds, and (3) a decrease in the amount of ammonia (the major product) formed which was more pronounced in the lower pH series. As a practical matter the beneficial effect of phosphate (comparable to that of sulfate) on the formation of gaseous-N products during the denitrification process is negated by the simultaneous inhibition of nitrate reduction.

In order to overcome the deleterious effect of phosphate on the denitrification process, the water must be treated (1) to remove the phosphate or (2) to render it inert with respect to the denitrification process. The second approach was tried initially since it would be a simpler solution from engineering and cost considerations. The most common chemicals for phosphate removal are iron salts, alum, and lime (Nesbitt, 1969) and, accordingly, these materials were tried as additives. In separate experiments, the addition of aluminum sulfate and ferric sulfate (Appendix XIV) to phosphate-containing nitrate solutions failed to lessen the phosphate inhibition of the denitrification process in that only 20 - 30% reduction of nitrate occurred. In further experiments using ferric iron (derived from recycle of half the precipitated solids from a preceding experiment) in conjunction with calcium hydroxide, less than 20% reduction of nitrate was observed with ammonia the principal product.

In the investigation of the other approach, namely separation of the precipitated phosphate before attempting denitrification, the majority of the experiments used recycled iron-containing solids in conjunction with calcium hydroxide for pH adjustment because of the obvious economic advantage if these reactants produced a practical pretreatment. From the data summarized in Appendix XV it is evident that a substantial percentage of the phosphate can be precipitated by treatment with recycled precipitate from the denitrification process. A problem seemingly inherent in the process is that at low level of phosphate (ca. 0.5 ppm P) the black Fe_3O_4 forms in the denitrification process, and this precipitate is not as efficient at removing phosphate as is the green $Fe_3(OH)_8$ which forms at higher phosphate levels (ca. 1 ppm P). Near the optimum range (4 - 6) for phosphate precipitation by ferric iron (Recht, 1970) the black Fe_3O_4 removed about 80% of the initial 10 ppm $PO_4^{\equiv}$-P while the green $Fe_3(OH)_8$ effected quantitative removal. Increased bascity (up to pH 9) had little effect on the amount of phosphate removed by recycled Fe_3O_4.

After quantitative removal of 10 ppm $PO_4^{\equiv}$-P by recycled green $Fe_3(OH)_8$, nitrate ion was readily and almost completely reduced. However, in these experiments the formation of gaseous-N products was significantly

less than expected, i.e., 40% rather than 70% conversion of nitrate. The remainder of the nitrogen was almost completely accounted for as ammonia. No explanation for this apparent anomaly has been found.

The use of lime for phosphate removal resulted in moderately successful subsequent denitrification. At lime dosages of 280 - 300 ppm CaO yields of gaseous-N products were near 70% (with 25 - 30% conversions of nitrate) with the remaining nitrogen found as ammonia. At higher lime dosages more nearly equal amounts of gaseous-N products and ammonia were observed without significant change in the amount of nitrate reduced.

Among the other precipitants for phosphate which were evaluated cursorily were ferrous iron and aluminum both of which are reported to be efficient at near neutral pH (Rippert, 1958). The solutions resulting after phosphate treatment with either ferrous iron alone or in combination with aluminum did not undergo denitrification readily. In each case only about 10% of the nitrate was reduced. Better nitrate reduction (about 55%) was achieved on solutions which had been treated with lanthanum (Recht, 1970) and in these experiments yields of gaseous-N products were about 75% with the remainder ammonia.

Effect of Carbonate

In the pH range (6 - 8) of interest for the denitrification process bicarbonate ion is the principal species with carbonate ion becoming more prevalent at higher pH values. At a carbonate concentration of 100 ppm reduction of nitrate ion was found to be 70 - 95% in the initial pH range 8 - 10 but formation of gaseous-N products was significant (55% yield and 52% conversion) only at the lower pH value. As noted previously (see section on Effect of Base) use of calcium hydroxide rather than sodium hydroxide resulted in a decrease in the amount of nitrate reduction (95% vs. 75%) at the same 100 ppm $CO_3^=$ concentration. With increasing carbonate concentration at an initial pH near 8 the extent of nitrate reduction decreased sharply. At 200 ppm carbonate only 25% of the nitrate was reduced (3 out of 4 experiments) and at 300 ppm carbonate the amount reduced had fallen to 16%. The yield of gaseous-N products was on the average just under half of the nitrate converted. The single exceptional experiment at the 200 ppm $CO_3^=$ level resembled those at the lower concentration in that the precipitate was the black Fe_3O_4 rather than the green $Fe_3(OH)_8$ observed in the other experiments with 200 (and higher) ppm $CO_3^=$. In that experiment the reduction of nitrate was over 50% and the yield of gaseous-N products was 77%. These different results from allegedly replicate experiments might have been the result of inhomogeneity in the calcium hydroxide slurry. Regardless of the cause, the results imply that at a concentration not far below 200 ppm $CO_3^=$ the inhibitory effect of this ion is minor.

An inspection of the potentiometric titration curves for $FeSO_4$-$CuSO_4$ solution containing $NaHCO_3$ (Figure 5) shows that at the low pH end the pH at which solids precipitate is not greatly different from that of $FeSO_4$-$CuSO_4$ (Figure 2) alone. At the high pH end the pH rises more gradually but sooner than when carbonate is absent. Thus, in the presence of carbonate one might predict that in the initial stages of the denitrification process larger amounts of ammonia would be formed at a given OH^-/Fe^{++} ratio but in the latter stages formation of gaseous-N products would not be inhibited.

It was noted in the experiments at 100 ppm $CO_3^=$ that the pH-time curve had the same shape as in the absence of carbonate (from the initial pH through a minimum, then a maximum, and then a decline to final value) but the time scale was extended about 4-fold (20 vs. 5 hrs.). Comparison of a series of 24 and 48 hour experiments showed no significant differences indicating reaction to be complete in less than 24 hours. The data are summarized in Appendix XVI.

Effect of Silicate and Other Inhibitors

Early in the experimental work it was noted that the time required for the change in color of the precipitate from green to black increased in a series of replicate experiments. Concomitantly a decrease in the amount of nitrate reduced was observed (see Appendix XVII). This time dependent phenomenon was rationalized as an inhibition caused by silicate or borate leached from the Pyrex glass storage buret used for 1 M NaOH. Although the conversion of nitrate to gaseous-N products decreased the yield remained essentially constant. The shape of the pH-time curve was normal but with the time scale extended even more than observed when carbonate was present.

Since silica is one of the most common constituents (at 20 - 30 ppm) of most natural as well as waste waters, the effectiveness of selected silicate precipitants (Appendix XVIII) and the effect on the denitrification process (Appendix XIV) were investigated. Of the sulfates of Al(III), Cu(II) and Fe(III) aluminum was most effective as a precipitant with 80% removal of an initial 25 ppm SiO_2. In the series of denitrification experiments the reduction of nitrate decreased, conversion to ammonia was high and constant, and both conversion and yield of gaseous-N products decreased as SiO_2 concentration increased. The time required for the precipitate to change color from green to black was generally less than half the time in the absence of silicate (1 - 2 hrs. vs. 4 - 5 hrs.) in keeping with the reported catalytic activity of silica in the air oxidation of ferrous hydroxide (Krause, 1958). These data are not consistent with the premise that silicate leached from the glass by the strong base was responsible for slowing of the denitrification process. Thus, borate remains as the suspected inhibitor. Insufficient time was available to determine the possible inhibitory effect of borate under controlled conditions.

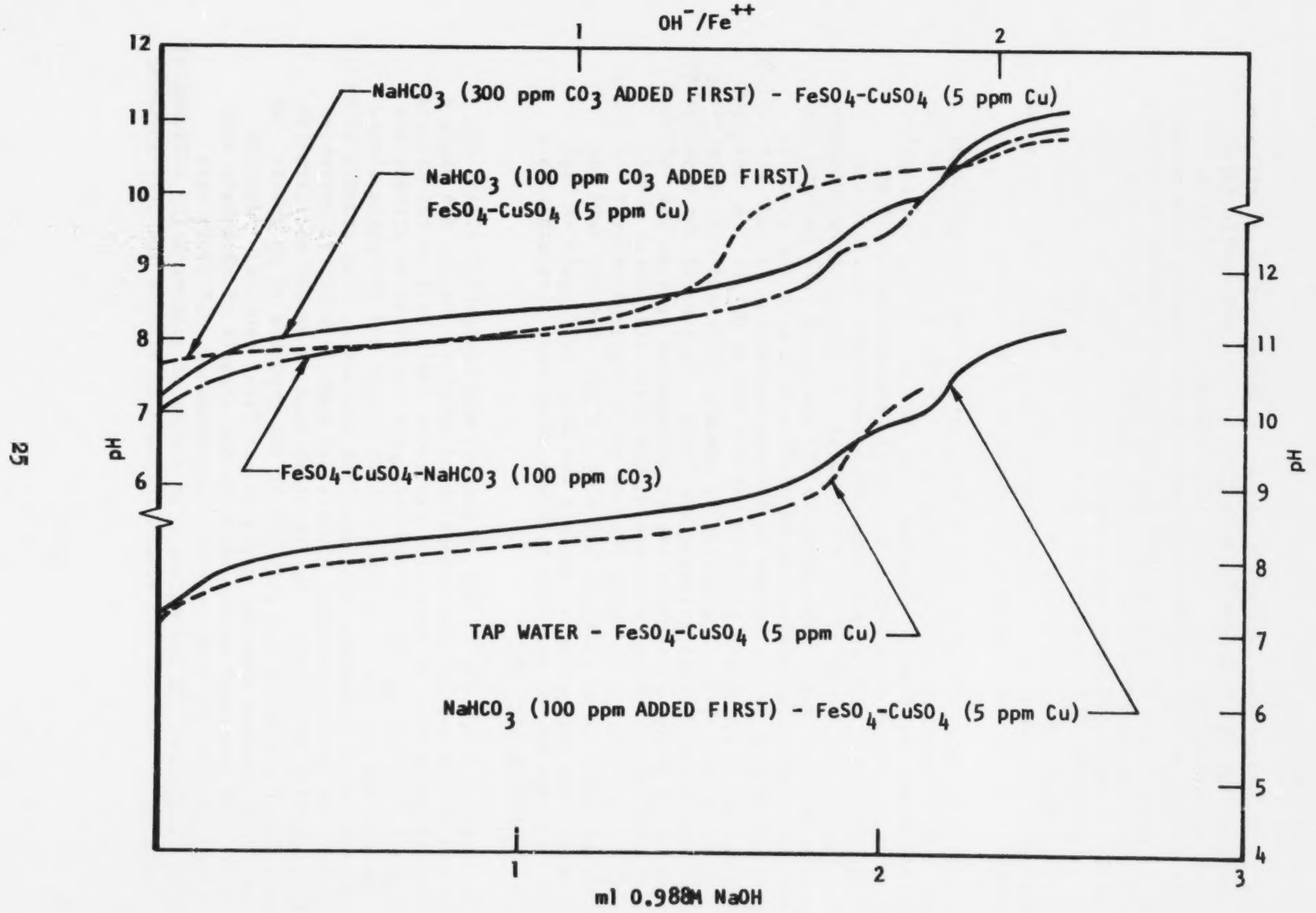


Figure 5. Potentiometric Titration Curves for $FeSO_4$-$CuSO_4$-$NaHCO_3$

REDUCTION OF NITRITE

Nitrite is the first intermediate produced in the reduction of nitrate. Its concentration was observed to be quite variable and particularly dependent on the OH^-/Fe^{++} mole ratio (see Appendix III). At high OH^-/Fe^{++} ratios nitrite together with ammonia was observed as a major product. A brief investigation of the uncatalyzed reduction of nitrite (Brown, 1967) was undertaken to determine whether the denitrification process might be broken into two steps--a catalyzed NO_3^- to NO_2^- step and an uncatalyzed NO_2^- to final products step--with improved efficiency in converting nitrate into N_2O and N_2. In addition, a study of the effect of phosphate on nitrite reduction in a copper-free system was conducted to aid in understanding the inhibitory mechanism.

The reported uncatalyzed reduction of both nitrite and hydroxylamine (Brown, 1967) formed ammonia quantitatively but the experimental conditions were much more drastic than had been used in the denitrification process, i.e., strong base (pH 14.2 - 14.7), concentrated oxidant (1400 ppm N), and either higher temperature or longer reaction time (110° C for 30 min. or 25° C for 1 - 3 days). A series of experiments at varying OH^-/Fe^{++} ratio (see Appendix XX) indicated that ammonia was the exclusive reduction product at $OH^-/Fe^{++} = 1.82$ with the quantity formed limited only by the amount of ferrous hydroxide. At $OH^-/Fe^{++} = 1.38$ the conversion to gaseous-N products was 83% and at $OH^-/Fe^{++} = 1.04$, 80% with yields of 83 - 91%. Conversion to ammonia decreased with decreasing OH^-/Fe^{++} ratio but no hydroxylamine was found. In some of the experiments the changes in pH and concentrations of nitrogenous species was followed as a function time. The pH remained on the basic side until about 90 - 95% of the nitrite had been reduced which required about 7 - 8 hours with normal addition of reagents but only 4 hours when the NaOH was added last. The conversion to ammonia was about half again as high (1.4 vs. 0.9 ppm NH_3-N) when the NaOH was added last presumably as a result of locally high pH.

The presence of 1 ppm $PO_4^{\equiv}$-P had an unusual and unexpected effect on the course of the uncatalyzed reduction of nitrite. On the one hand, a significant inhibition of reduction was noted (only half of the nitrite was reduced) indicating that in the catalyzed reduction of nitrate the poor results are not due to interaction of copper and phosphate alone. The interaction of phosphate with the iron hydroxides thus appears to be significant in the reduction of nitrite and most probably is operative in the reduction of nitrate. On the other hand, a marked acceleration in the rate of reduction was effected by the presence of phosphate. At the end of 30 minutes when the reaction was first sampled, reduction of nitrite had proceeded to 52% while in the absence of phosphate only 13% of the nitrite had been reduced. Approximately 2.5 hours were required to achieve 50% reduction. The yields of gaseous-N (by difference) were comparable. Whether the slight increase in nitrite and corresponding

decrease in gaseous-N during the 4 hour reaction time is real or due to analytical error was not resolved.

DENITRIFICATION REACTION TIME AND ITS APPLICATION TO A DYNAMIC SYSTEM

In order to optimize the denitrification process and use it in practical water treatment applications the minimum reaction time must be determined. Aside from a single experiment of 19.5 hours duration (virtually indistinguishable from 24-hour runs) only a few experiments of 1 -2 hour duration were conducted (see Appendix VIII) in the early part of the program. Each of these experiments run at the high ratio of OH^-/Fe^{++}=1.83 indicated with normal addition of reagents that a fairly rapid (< 1 hour) reduction of nitrate to nitrite occurred followed by a slow and incomplete conversion to gaseous-N products.

In order to obtain further data on the time dependent course of the denitrification process a number of experiments were scaled up to permit multiple sampling for analysis. In one of these experiments all of the reagents were added initially in the usual manner while in two others the coprecipitated $Fe(OH)_2$-$Cu(OH)_2$ mixture was added continuously during the first 4 hours of the reaction. The data summarized in Appendix XXI for the conventional experiment confirmed the previously observed formation of ammonia and nitrite in the first hour or so followed by conversion of nitrite to gaseous-N products during the next 4 - 5 hours. At the low OH^-/Fe^{++} ratio (1.37) used the pH fell within 3 hours to 5.72 which slowed reduction of nitrate to a virtual standstill near 60% conversion. An attempt to restart the reduction by addition of $NaHCO_3$ to raise the pH was unsuccessful.

The continuous addition of a preformed $Fe(OH)_2$-$Cu(OH)_2$ mixture to a nitrate solution resulted in formation of higher than usual amounts of ammonia. Presumably the reduction to ammonia was favored over formation of gaseous-N products by the presence of the black solids formed early in the experiment (vide supra - Catalyst Evaluation). Again the conversion of nitrate was poor presumably as a result of too rapid a drop in the pH but the yield of gaseous-N products was high (87%).

The efforts to effect the reduction of nitrate in a flow system were at best preliminary and clearly indicated that flowrates greater than 50 - 100 ml/hr. will be required to obtain reliable data. Despite the mechanical problems associated with control of the low flowrates the continuous reactor with recirculating solids was effective in achieving reduction of nitrate (see Appendix XXII, Experiment 277A - 277V).

The pH remained at 7.84 ± 0.04 during the time samples A-G were taken. The high concentration of NO_3^--N in the effluent (ca. 65% of influent) was interpreted as the result of too short a retention time (< 2 hrs.) in contact with the iron-copper solids. That the major reduction product

was ammonia was attributed to the presence of the aged solids and perhaps too high a pH. Accordingly, the flowrates were adjusted downward for samples H-K. In this series the pH was indicated to be in the range 7.3 - 7.4 but the reliability of these valves is questionable because of a subsequent electrode failure. The relative flowrates of the reagents would indicate the pH to be of the correct order of magnitude. The formation of gaseous-N products was 10-13% indicating the doubled retention time was beneficial. The higher proportion of unreacted NO_3^- resulted from the relatively higher NO_3^- flowrate (a decreased Fe^{++}/NO_3^- ratio) and the high proportion of the nitrogen reduced to ammonia.

An adjustment of the nitrate flowrates and the NaOH resulted in a low influent nitrate concentration and a higher OH^-/Fe^{++} ratio. These conditions were found to give over 90% reduction of nitrate but the proportion of ammonia remained high. Gaseous-N products increased to 28% accompanied by 27% nitrite (which should convert to gaseous-N products with a longer retention time). The conditions for samples M-Q gave results similar to those obtained initially.

Of particular significance was the consistent formation of ammonia in relatively high yield similar to that observed when recycled solids were used as the catalyst source. To confirm this effect in the flow system the flowrates were left undisturbed while the black sludge was flushed from the reactor. The residual solids were dissolved in concentrated hydrochloric acid and the reactor was flushed with distilled water. It will be noted that in samples R-V (obtained between 6.5 - 13 hrs. after flushing the reactor with water and an approximate eight-hour retention time) that the NH_3-N concentration rose but not as high as before (using the NO_3-N concentration as an internal standard). These data when considered with the pH time dependence suggest that a longer residence time (estimated 5 - 6 hours) would be beneficial in a reactor in which solids are not retained.

Accordingly, a stirred tubular flow reactor was employed in a brief attempt to obtain some data on this design. Limitations such as flowrate control set the residence time at less than one hour so that an effort was made to effect reduction of nitrate to nitrite only. Such data as might be obtained would have a bearing on the feasibility of separating the denitrification process into a two-step process where only the first step is catalyzed. The data summarized in Appendix XXIII indicated that 30 - 35% reduction of nitrate was achieved in 0.6 - 0.8 hour with NO_2^-/NH_3 ratio of about 3. It would appear from the single experiment that separation of the denitrification process into two steps would not be practical but that this reactor design would be useful for a single step process.

PRELIMINARY EVALUATION OF THE DENITRIFICATION PROCESS USING BOTH TAP WATER AND SECONDARY EFFLUENT

Since the tap water contained both carbonate and silicate and the secondary effluent contained phosphate in addition, a preliminary treatment was given to the samples before denitrification was attempted. In all nine anion removal pretreatment processes were used in an effort to obtain data which would enable direct comparison of the efficiency of the process in the two media.

Pretreatment with varying amounts of lime (process A - see Appendix XXIV) alone for short times (0.25 - 0.5 hr.) at low temperatures (70 - 85° F) removed over 90% of the phosphate and presumably some carbonate as well although no analyses for the latter were made. The subsequent reduction of nitrate in both tap water and effluent was low (5 - 17%) generally with more gaseous-N products formed than ammonia. The yield of gaseous-N products was generally near 60%.

The next two pretreatments involving ferric iron were evaluated because recycled iron solids containing ferric iron resulted in higher than normal conversions of nitrate to ammonia (see Appendix XV). Pretreatment with ferric sulfate alone (process C) or preceded by lime treatment (process B) were ineffective in that nitrate reduction in effluent was poor (6 - 13%) and the yields of gaseous-N products were erratic. Apparently, the previously observed increase in ammonia at the expense of gaseous-N products results from the presence of the copper-containing Fe_3O_4 and not just ferric iron. Pretreatment of effluent with ferric sulfate followed by lime with (process D) or without (process E) prior acidification resulted in moderate improvements in both the amount of nitrate reduced (23 - 28%) and the conversion to gaseous-N products (26 - 34%), but the conversion to ammonia was increased as well.

An acidification pretreatment to remove carbonate was used on tap water (process F) and on effluent (process H) which included subsequent lime treatment to decrease phosphate concentration. With this treatment, subsequent nitrate reduction in tap water and effluent, respectively, was increased to 49% and 45% but ammonia was found as the major reduction product (33% conversion) with 16% and 27% conversion to gaseous-N products.

In an attempt to improve the denitrification over that obtained with the liming pretreatment, additional contacting with magnesium oxide at 85° F and 194° F (process G) was evaluated assuming that silicate removal would be beneficial. At the lower temperature no changes were apparent when compared with liming alone (process A) for either tap water or effluent. At the higher temperature, reduction was increased to 55%, most of which was converted to ammonia (42%) in tap water while in effluent the reduction was markedly inhibited (only 5% reduction of nitrate).

Inspection of the initial and final phosphate concentrations indicates that the solids precipitated during the course of the denitrification experiments are quite effective in removing this anion from solution. It is not unreasonable to assume that the concentration of other anionic species, such as carbonate, borate, silicate, etc., might be decreased simultaneously. If inhibitory substances, either known or unknown, were removed, then a second denitrification reaction should proceed more efficiently in the same solution. Several experiments were conducted to evaluate this anion removal process (process I). The following results were obtained in tap water in the second denitrification for the indicated first pretreatment: (a) no pretreatment, slight improvement in nitrate reduction but marked decrease in conversion to ammonia with corresponding increase in gaseous-N products, (b) lime pretreatment (process A), nitrate reduction increased 2.5 times but conversions to ammonia, nitrite and gaseous-N products all increased, and (c) lime plus hot MgO pretreatment (process G), decreased nitrate reduction but more gaseous-N products formed at the expense of ammonia.

Similar double denitrification experiments starting with secondary effluent gave the following results: (a) lime pretreatment (process A) nitrate reduction while still low (34%)had doubled as did formation of gaseous-N products with a decrease in conversion to ammonia, and (b) lime plus hot MgO pretreatment (process G), a large increase in nitrate reduction (from 5% to 54%) with low conversion to ammonia (9%) and high conversion to gaseous-N products (43%).

The data imply that some inhibitory substances have been removed by the iron-containing solids formed during the denitrification process but further experiments will be required to identify these species.

ANALYTICAL SUPPORT

The analytical chemistry support activities during this program consisted primarily of routine analyses for nitrate, nitrite, and ammonia. Additional routine analyses were carried out for copper, phosphate, and silica content. From time to time some special analytical problems requiring the application of non-routine analytical methods were performed primarily to determine whether there were nitrogenous species formed other than nitrate, nitrite, or ammonia during the denitrification process. Analyses for sulfate and chloride were done conductometrically.

Routine Analyses

Ultraviolet Spectrophotometric Method for Nitrate and Nitrite Ions. The analysis procedure for nitrate and nitrite was virtually the same as used in the feasibility study (Gunderloy, 1968). The absorbances at 200 mμ before and after treatment of sample with sulfamic acid were determined. The total absorbance is the measure of NO_3^- and NO_2^-, while the decrease as a result of sulfamic acid addition is a measure of NO_2^-. Interference effects of iron, sulfate, chloride, and sulfamic acid were determined and used to correct for these species when necessary.

Tests with nitrate and nitrite samples at the 0 - 10 ppm N level indicate an accuracy of ± 0.2 ppm for nitrate ion. Because of the lower extinction coefficient of nitrite ion, the accuracy for it is only ± 0.4 ppm.

Ammonia Distillation Method. Analysis for ammonia was performed by the Kjeldahl distillation method used in the feasibility study (Gunderloy, 1968).

Copper. Copper at the part per million level was determined by atomic adsorption spectrophotometry using a Perkin-Elmer Model 303 instrument. The conditions of analysis are described in the manufacturer's literature (anonymous, 1966).

Silica. Soluble silicates were determined by the colorimetric molybdosilicate method (Method B) described in the Standard Methods for the Examination of Water (anonymous, 1965), using the Cary 14 recording spectrophotometer. Method A, the gravimetric method was used to standardize the sodium silicate standard solutions. Phosphate ion up to 10 ppm P was found not to interfere with the colorimetric method.

Phosphate. The analysis for phosphate was performed by the molybdenum blue spectrophotometric method using the Cary 14 recording spectrophotometer (Furman, 1962).

Special Analytical Problems

Presence of Nitrogenous Species Other Than NO_3^-, NO_2^-, and NH_3. A comparison of the sum of the nitrogen found by separate analyses for NO_3^-, NO_2^-, and NH_3 with a total nitrogen method was made. Two methods for the determination of total nitrogen were investigated. The purpose was to convert all nitrogen-containing species, except dissolved N_2 or N_2O to a single oxidation state before analysis.

The first method was an oxidation using hydrogen peroxide. Standard solutions of nitrite ion and ammonium ion were run. Nitrite ion standards were oxidized quantitatively to nitrate, but ammonium ion remained unchanged. When experimental samples were analyzed by the peroxide oxidation, however, it appeared that some nitrite remained unoxidized. The oxidation procedure, therefore, was not considered satisfactory.

The second approach was a reduction method using ferrous sulfate in highly alkaline media with silver sulfate catalyst to reduce all nitrogenous species to NH_3. Total nitrogen by the reduction method compared favorable with the sum of nitrogen found by separate analyses for NO_3^-, NO_2^-, and NH_3 for experiments 25 and 26 (Table I). The following procedure was used for both standards and experimental samples.

A 20 ml aliquot of sample was added to the reaction vessel followed by 5 ml of 50% NaOH solution, 10 ml of saturated Ag_2SO_4 solution, and enough

TABLE I

REDUCTION OF NITROGENOUS SPECIES TO AMMONIA

Sample	µg N Added	N Found by Standard Methods ppm, NH_3+NO_2^-+NO_3^-	N Found by Reduction (µg or ppm)
Nitrate Standard	195.0	-	184 µg
	198.0	-	198 µg
Hydroxylamine Hydrochloride Standard	200.6	-	200.7 µg
	200.6	-	201.3 µg
	200.6[a]	-	8.0 µg
Nitrite Standard	200.0	-	200.6 µg
	200.0	-	190.0 µg
Experiment 25	-	3.04	2.94 ppm
	-	3.04	3.00 ppm
Experiment 26	-	3.57	3.59 ppm

[a] No $FeSO_4$ added

$FeSO_4$ solution to provide a two-fold excess to convert NO_3^- (10 ppm N) to NH_3. The solution was heated to incipient boiling and held for 30 minutes after which it was distilled into boric acid solution as is done in a routine NH_3 determination. Nitrite and hydroxylamine were found to be reduced without the 30 minute heating time and without the addition of Ag_2SO_4 catalyst.

A method for the determination of hydroxyamine was developed from reported information (Nunes, 1970). Hydroxylamine was reported to be converted to nitrous oxide by reacting with copper(II) chloride in acidified solution. Removal of nitrous oxide was accomplished by boiling the solution. The analytical method developed was a two-step procedure. One aliquot of the sample was reduced to ammonia using excess $FeSO_4$ solution. Upon Kjeldahl distillation, this gave the total ammonia and hydroxylamine present. A second aliquot was treated with excess $CuCl_2$ solution, acidified and boiled one hour to destroy the hydroxylamine after which the ammonia was Kjeldahl distilled from basic solution into boric acid and titrated with standard acid. The difference between the first and second titrations was a measure of the hydroxylamine. Hydroxylamine was found not to distill with ammonia in the standard Kjeldahl distillation.

Experiments 278 and 279 were analyzed by this method. Each of these solutions was found to contain nitrite-N by the uv method. Therefore, the nitrite ion was destroyed by the addition of sulfamic acid prior to analysis in Step 1. In Step 2, the nitrite ion was removed during the one hour boiling. No hydroxylamine was found in either Sample 278 or 279. Accuracy on known mixtures containing all possible species, NO_3^-, NO_2^-, NH_3, and hydroxylamine was not as good as desired (Table II), but was considered adequate for the information desired in Experiments 278 and 279.

Sulfate and Chloride Analyses. A sample containing approximately 10 mmoles of $SO_4^=$ was diluted to 5 ml with water and 3 ml of tetrahydrofuran was added. The conductivity of the solution was recorded on a stripchart recorder as it was titrated automatically with 0.010 M $Ba(OCOCH_3)_2$. Extrapolation of the straight portions of the graph (i.e., the decreasing conductivity as $BaSO_4$ formed and the increasing conductivity as $Ba(OCOCH_3)_2$ concentration increased) gave the time to precipitate all the sulfate. Calibration was with standardized 0.010 M Na_2SO_4 solution. In the samples contained calcium ion, it was replaced with sodium by ion exchange before titration.

Chloride ion was determined in a similar manner by titrating the samples with 0.010 M $AgNO_3$. Tetrahydrofuran was not used nor was it necessary to remove calcium ion from the solutions.

TABLE II

DETERMINATION OF HYDROXYLAMINE AND

AMMONIA IN KNOWN MIXTURES

MIXTURE A	MIXTURE B
0.25 ppm NO_3^-	0.25 ppm NO_3^-
0.50 ppm NO_2^-	0.50 ppm NO_2^-
1.4 ppm NH_3	1.4 ppm NH_3
0.0 ppm NH_2OH	1.0 ppm NH_2OH

Mixture	NH_3-N, ppm		NH_2OH-N, ppm		Total-N, ppm	
	Added	Found	Added	Found	Added	Found
A	1.4	1.6	0.0	-0.2	1.4	1.4
B	1.4	1.5	1.0	0.9	2.4	2.4

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APPENDIX I

REAGENT STOCK SOLUTIONS

Reagent	Concentration	
	Molarity	ppm
KNO_3	0.1428	2,000 N
$FeSO_4$ / H_2SO_4	0.5712 0.0022	55,080 $SO_4^=$ 31,900 Fe^{++}
$FeCl_2$	1.1424	81,000 Cl^- 31,900 Fe^{++}
$CuSO_4$	0.0157	1,000 Cu^{++} 1,510 $SO_4^=$
$CuCl_2$	0.0157	1,000 Cu^{++} 1,120 Cl^-
Na_2HPO_4	0.0646	2,000 P
$NaHCO_3$	0.3333	20,000 $CO_3^=$
Na_2SiO_3	0.0162	972 SiO_2
NaOH	0.98	--
$Ca(OH)_2$ (1% slurry)	0.1337	--
$NaNO_2$ [a]	0.0144	202 N

[a] Never stored over 4 days

APPENDIX II

IDENTIFICATION OF GASEOUS-N COMPOUNDS

Experiment No.	pH		Nitrogen Material Balance, ppm							Mass Spectrometer Analysis						
						Gaseous-N Compounds				Gas Volume, cc	Mole, percent					
	Initial	Final	NH_3-N	NO_3^--N	NO_2^--N	N_2O-N	N_2-N	NO-N	Unidentified (by difference)		He	N_2O	N_2	NO	O_2	CO_2
16[a]	8.27	7.24	1.9	2.4	-1.3	1.0	(a)	--	6.0	3.61	89.0	4.2	4.7	--	1.6	0.5
18[a]	8.10	6.81	1.6	4.9	0.3	0.9	0.9	--	1.4	3.43	87.8	4.4	7.0	--	0.7	0.1
25	7.87	5.61	1.9	1.1	0.1	(b)	(b)	--	6.9	3.95	--	(b)	(b)	--	--	--
29[c]	--	--	--	--	--	--	--	--	--	3.95	97.7	--	2.3	--	--	--
30	8.40	5.47	2.0	1.0	0.1	3.8	2.6	--	0.5	4.81	78.8	12.5	8.7	--	--	--
31	8.42	5.42	1.9	1.4	0.5	3.5	2.4	0.1	0.2	4.48	75.3	12.2	11.0	0.8	0.6	--

Fixed Conditions:

Reactor ullage	2.53 cc
Initial NO_3^--N concentration (1.000 ml 0.1428 M KNO_3/200 ml)	10 ppm
Fe^{++}/NO_3^- mole ratio (2.000 ml 0.5712 M $FeSO_4$ + 0.0022 M H_2SO_4/200 ml)	8
Catalyst concentration (1.000 ml 0.0157 M $CuSO_4$/200 ml)	5 ppm Cu^{++}
pH Adjustment (1.70 ml 0.98 ± 0.01 M NaOH/200 ml)	
Reaction time	24 hours
Temperature	85 F
Atmosphere	Helium

(a) NaOH stock solution used had been in contact with borosilicate glass for 28 days (Experiment 16) and 50 days (Experiment 18) resulting in an inhibition of the denitrification process

(b) Quantitative data not available due to malfunction of mass spectrometer and subsequent loss of sample

(c) Blank (No KNO_3 used) run to determine baseline value for helium using improved degassing procedure (used in Experiments 30 and 31)

APPENDIX III

EFFECT OF INITIAL pH ON DENITRIFICATION

Experiment No.	Volume 0.98N NaOH Solution, ml/200ml	OH^-/Fe^{++} Mole Ratio	pH		Nitrogen Material Balance, ppm				Gaseous-N, Percent Yield	Final $SO_4^=$ Concentration, ppm(a)
			Initial	Final	NH_3-N	NO_3^--N	NO_2^--N	Gaseous-N (by difference)		
1	1.130	0.97	8.80	5.60	1.4	5.6	-0.4	3.4	77	--
2	1.295	1.11	8.00	5.41	1.8	3.7	0.1	4.4	70	--
3	1.950	1.67	9.50	5.66	3.8	2.1	1.9	2.2	28	--
4	1.950	1.67	8.45	5.60	4.3	1.5	0.1	4.1	48	--
19	2.400	2.06	10.96	10.70	4.0	0.0	5.9	0.1	1	--
20	2.400	2.06	10.94	10.78	4.5	0.0	5.3	0.2	2	--
21	2.400	2.06	10.97	10.79	4.6	0.0	5.0	0.4	4	--
5	2.200	1.89	10.46	7.81	4.9	0.5	4.5	0.1	1	541
6	2.200	1.89	10.60	8.62	5.2	0.4	6.1	-1.7	--	542
13	2.200	1.89	8.92	8.84	5.1	0.1	2.4	2.4	24	543
14	2.200	1.89	8.57	8.72	4.9	0.1	4.8	0.2	2	545
15	2.200	1.89	8.77	8.56	5.1	0.0	4.3	0.6	6	545
219	2.00	1.72	8.50	3.96	4.6	1.1	4.2	0.1	1	--
220	1.95	1.67	8.25	5.02	3.9	0.8	0.5	4.8	52	--
10	1.950	1.67	8.40	5.66	3.2	0.6	0.7	5.5	59	536
11	1.950	1.67	8.30	5.29	3.4	0.8	2.0	3.8	41	536
12	1.950	1.67	8.30	5.10	3.1	0.6	0.3	6.1	65	536
7	1.700	1.46	8.15	5.30	1.8	0.8	-0.3	7.7	84	525
8	1.700	1.46	8.00	5.30	1.8	0.7	0.3	6.2	67	528
9	1.700	1.46	8.04	5.53	1.9	0.7	0.5	6.9	74	528
273	1.20	1.03	7.40	5.20	0.8	3.9	0.0	5.3	87	--

Fixed Conditions:

Initial NO_2^--N concentration (1.000ml 0.1428N KNO_2/200ml)	10 ppm
Fe^{++}/NO_3^- mole ratio (2.000ml 0.5712N $FeSO_4$ + 0.0022N H_2SO_4/200ml)	8
Catalyst concentration (1.000ml 0.0157M $CuSO_4$/200ml	5 ppm Cu^{++}
Reaction Time	24 hours
Temperature	85°F
Atmosphere	Helium

(a) Initial $SO_4^=$ concentration, 558 ppm

APPENDIX IV

EFFECT OF THE BASE AND VARYING $FeSO_4/FeCl_2$ MOLE RATIO

Experiment No.	$\frac{FeSO_4}{FeCl_2}$ Ratio	Base[a]	OH^-/Fe^{++} Mole Ratio	pH		Nitrogen Material Balance, ppm				Gaseous-N, Percent Yield	Anion Concentration, ppm	
				Initial	Final	NH_3-N	NO_3^--N	NO_2^--N	Gaseous-N (by difference)		$SO_4^=$ Final/ Initial	Cl^- Final/ Initial
145	∞	NaOH	1.46	8.42	5.35	2.1	0.4	0.5	7.2	75	503/558	---/0
146	∞	NaOH	1.46	8.34	5.31	2.1	0.4	0.3	7.2	75	500/558	---/0
156	∞	$Ca(OH)_2$	1.45	8.23	5.02	1.5	2.0	0.3	6.2	78	487/558	---/0
157	∞	$Ca(OH)_2$	1.45	8.31	5.45	1.7	1.6	0.1	6.6	79	477/558	---/0
147	3	NaOH	1.46	8.36	5.31	1.7	0.4	0.6	7.3	76	376/421	105/101
148	3	NaOH	1.46	8.33	5.21	1.9	0.4	0.0	7.7	80	380/421	110/101
158	3	$Ca(OH)_2$	1.45	8.31	5.84	1.9	1.8	0.5	5.8	71	368/421	105/101
159	3	$Ca(OH)_2$	1.45	8.23	5.42	1.7	1.4	0.3	6.6	77	346/421	104/101
149	1	NaOH	1.46	8.20	5.43	1.7	0.8	0.6	6.9	75	250/283	201/203
150	1	NaOH	1.46	8.13	5.35	1.8	0.8	0.0	7.4	80	254/283	201/203
160	1	$Ca(OH)_2$	1.45	8.26	5.35	1.1	2.7	0.0	6.2	85	233/283	200/203
161	1	$Ca(OH)_2$	1.45	8.26	5.86	1.7	1.9	0.7	5.7	70	228/283	195/203
151	0.33	NaOH	1.46	8.12	5.78	1.9	1.1	0.8	6.2	70	125/144	293/304
152	0.33	NaOH	1.46	8.13	5.72	2.0	1.1	0.6	6.3	71	125/144	293/304
162	0.33	$Ca(OH)_2$	1.45	8.33	5.91	1.8	2.0	0.8	5.4	68	116/144	288/304
163	0.33	$Ca(OH)_2$	1.45	8.32	5.80	2.1	2.3	0.4	5.2	68	117/144	293/304
153	0	NaOH	1.46	8.31	5.34	3.6	3.5	0.2	2.7	42	---/7.6	381/405
154	0	NaOH	1.46	8.36	5.25	3.5	3.6	0.0	2.9	45	---/7.6	381/405
164	0	$Ca(OH)_2$	1.45	8.33	5.56	2.7	4.6	0.3	2.4	44	---/7.6	386/405
165	0	$Ca(OH)_2$	1.45	8.30	5.64	3.1	4.3	0.0	2.6	46	---/7.6	383/405

Fixed Conditions:

Initial NO_3^--N concentration (1.000 ml 0.1428N KNO_3/200 ml)	10 ppm
Fe^{++}/NO_3^- mole ratio (ml $FeSO_4$ + 2.000 - 2[ml$FeCl_2$]) using 2.000 ml 0.5712N $FeSO_4$ + 0.0022N H_2SO_4/200 ml or 1.000 ml 1.1424N $FeCl_2$/200 ml)	8
Catalyst concentration (1.000 ml 0.0157N $CuSO_4$/200 ml)	5 ppm Cu^{++}
Reaction time	24 hours
Temperature	85°F
Atmosphere	Helium

(a)pH adjusted with either 1.70 ml 0.98N NaOH or 6.20 ml 1 percent $Ca(OH)_2$ slurry

APPENDIX V

EFFECT OF Fe^{++}/NO_3^- MOLE RATIO USING $FeSO_4$

Experiment No.	Fe^{++}/NO_3^- Mole Ratio	Volume 0.98M NaOH, ml	OH^-/Fe^{++} Mole Ratio	pH		Nitrogen Material Balance, ppm				Gaseous-N, Percent Yield
				Initial	Final	NH_3-N	NO_3^--N	NO_2^--N	Gaseous-N (By Difference)	
198	16	4.56[a]	1.96	8.21	8.07	9.4	0.2	0.1	0.3	3
199	16	4.72[a]	2.02	8.39	8.62	8.4	0.1	0.0	1.5	15
38	12	1.80	1.03	8.04	5.24	2.2	1.1	0.2	6.5	73
39	12	1.80	1.03	8.10	5.08	2.2	1.6	0.1	6.1	73
32	10	1.70	1.17	8.34	5.35	2.4	1.5	0.4	5.7	67
33	10	1.70	1.17	8.17	5.35	2.0	1.5	0.2	6.3	74
271[b]	8	1.85	1.39	7.72	5.42	3.0	0.7	0.2	6.1	66
7	8	1.700	1.46	8.15	5.30	1.8	0.8	-0.3	7.7	84
8	8	1.700	1.46	8.00	5.30	1.8	0.8	0.3	6.2	78
9	8	1.700	1.46	8.04	5.53	1.9	0.7	0.5	6.9	74
145	8	1.70	1.46	8.42	5.35	2.1	0.4	0.3	7.2	75
146	8	1.70	1.46	8.34	5.31	2.1	0.4	0.3	7.2	75
156	8	1.66[a]	1.45	8.23	5.02	1.5	2.0	0.3	6.2	78
157	8	1.66[a]	1.45	8.31	5.45	1.7	1.6	0.1	6.6	79
155	8	0.88	0.50	8.17	5.28	0.8	7.7	0.7	0.8	35
34	6	1.60	1.83	8.82	4.12	2.0	1.4	5.0	1.6	19
37	6	1.60	1.83	8.84	5.78	2.7	0.6	3.3	3.4	36
41	6	1.60	1.83	8.60	5.30	2.7	0.6	5.2	1.5	16
60	6	1.60	1.83	8.80	5.69	2.8	2.1	2.0	3.1	39
61	6	1.60	1.83	8.78	6.20	2.9	1.7	3.2	2.2	27
40[c]	6	1.60	1.83	8.76	6.12	2.6	0.4	6.3	0.7	7
85[d]	6	1.60	1.83	8.71	7.90	1.7	0.5	7.3	0.5	5
87[d]	6	1.60	1.83	8.79	6.40	2.6	0.2	6.9	0.3	3
35	6	1.80	1.72	8.40	5.35	2.4	1.9	0.5	5.5	68
36	6	1.80	1.72	8.52	5.40	2.3	1.3	0.4	6.0	69
68	5	1.25	1.72	8.48	4.44	1.9	2.1	1.6	4.4	56
69	5	1.25	1.72	8.32	5.22	1.9	1.6	0.9	5.6	67
64	4	1.00	1.72	8.48	5.51	0.8	2.3	1.6	5.3	69
65	4	1.00	1.72	8.45	4.96	1.1	2.6	1.4	4.9	66
70	3	0.75	1.72	8.30	4.18	0.6	4.5	1.2	3.7	67
71	3	0.75	1.72	8.29	4.34	0.6	4.4	2.6	2.4	43
66	2	0.50	1.72	8.58	5.84	0.2	6.1	1.6	2.1	54
67	2	0.50	1.72	8.26	5.45	0.2	7.2	2.5	0.1	4

Fixed Conditions:

Initial NO_3^--N concentration (1.000 ml 0.1428N KNO_3/200 ml)	10 ppm
Fe^{++} concentration (0.280 ml 0.8712 M $FeSO_4$ + 0.0022M H_2SO_4/200 ml for each unit value of Fe^{++}/NO_3^- mole ratio)	
Catalyst concentration (1.000 ml 0.0157M $CuSO_4$/200 ml)	5 ppm Cu^{++}
Reaction time	24 hours
Temperature	85 F
Atmosphere.	Helium

(a) 1 percent $Ca(OH)_2$ slurry used; calculated ml 0.98 M NaOH derived by multiplication of ml 1 percent $Ca(OH)_2$ by 0.368
(b) 19.5 hour reaction time
(c) 1.5 hour reaction time
(d) 1.0 hour reaction time

APPENDIX VI

EFFECT OF Fe^{++}/NO_3 MOLE RATIO USING $FeCl_2$

Experiment No.	Fe^{++}/NO_3^- Mole Ratio	Volume 0.98M NaOH,ml	OH^-/Fe^{++} Mole Ratio	pH		Nitrogen Material Balance, ppm				Gaseous-N, Percent Yield
				Initial	Final	NH_3-N	NO_3^--N	NO_2^--N	Gaseous-N (by difference)	
90	16	2.50	1.07	8.06	5.83	7.8	4.5[a]	0.8[a]	-3.1	-
91	8	1.80	1.54	8.29	5.59	5.5	4.3	0.0	0.2	4
92	8	1.80	1.54	8.20	5.52	5.2	4.5	0.2	0.1	2
153[b]	8	1.70	1.46	8.31	5.34	3.6	3.5	0.2	2.7	42
154[b]	8	1.70	1.46	8.36	5.25	3.5	3.6	0.0	2.9	45
164[b]	8	1.66[c]	1.45	8.33	3.56	2.7	4.6	0.3	2.4	44
165[b]	8	1.66[c]	1.45	8.30	5.64	3.1	4.3	0.0	2.6	46
93	6	1.30	1.49	8.26	5.29	3.3	5.6	-0.2	1.3	30
94	6	1.30	1.49	8.12	5.36	3.3	5.7	0.1	0.9	21
95	5	1.10	1.51	8.17	5.00	2.8	6.3	-0.2	1.1	30
96	5	1.10	1.51	8.12	4.96	2.5	6.5	-0.1	1.1	31
97	4	0.70	1.20	8.11	4.85	1.2	7.5	-0.6	1.9	76
98	4	0.70	1.20	8.02	4.76	1.3	7.5	-0.7	1.9	76
99	3	0.60	1.37	8.09	4.95	0.9	7.5	-0.4	2.0	80
100	3	0.60	1.37	8.07	4.97	0.8	7.5	-0.4	2.1	84
101[a]	2	0.35	1.20	8.16	4.19	0.3	8.7[a]	-0.4[a]	1.4	107
102[a]	2	0.35	1.20	7.96	3.99	0.3	9.4[a]	-0.1[a]	0.4	67

Fixed Conditions:

Initial NO_3-N concentration (1.000 ml 0.1428M KNO_3/200 ml)	10 ppm
Fe^{++} concentration (0.125 ml 1.1424M $FeCl_2$/200 ml for each unit value of Fe^{++}/NO_3^- mole ratio)	
Catalyst concentration (1.000 ml 0.0157M $CuCl_2$/200 ml)	5 ppm Cu^{++}
Reaction Time	24 hours
Temperature	85°F
Atmosphere	Helium

(a) Dark brown supernatant gave high background in spectrophotometric analysis for NO_3^- and NO_2^- due to inability to balance the instrument.

(b) 1.000 ml 0.0157M $CuSO_4$/200 ml used in lieu of equivalent amount of $CuCl_2$.

(c) 1 percent $Ca(OH)_2$ slurry used; calculated ml 0.98M NaOH derived by multiplication of ml 1 percent $Ca(OH)_2$ by 0.268.

APPENDIX VII

CATALYST CONCENTRATION EFFECT

Experiment No.	Cu^{++} Concentration, ppm(a)	pH		Nitrogen Material Balance, ppm			
		Initial	Final	NH_3–N	NO_3^-–N	NO_2^-–N	Gaseous-N (by difference)
7	5	8.15	5.30	1.8	0.8	-0.3	7.7
8	5	8.00	5.30	1.8	0.7	0.3	6.2
9	5	8.04	5.53	1.9	0.7	0.5	6.9
42	4	8.46	5.41	2.0	1.0	-0.2	7.2
43	4	8.36	5.35	2.1	0.6	0.2	7.1
44	3	8.30	3.84	1.8	1.2	0.5	6.5
45	3	8.30	5.52	2.1	1.0	0.0	6.9
46	2	8.32	5.38	1.1	0.6	0.6	7.7
47	2	8.30	5.44	2.1	0.4	0.2	7.3
50	1	8.32	5.66	2.2	1.0	0.3	6.5
51	1	8.33	5.45	2.2	1.2	0.1	6.5
52	0.5	8.44	5.73	1.9	3.3	0.0	4.8
53	0.5	8.24	7.50	2.4	3.7	1.2	2.7
54	0.05(b)	8.36	7.64	0.5	9.5	0.0	0.0
55	0.05(b)	8.33	7.74	0.5	9.5	0.5	-0.5
48	(c)	8.34	7.28	1.1	8.8	-0.2	0.3
49	(c)	8.35	7.91	1.2	8.1	0.5	0.2

Fixed Conditions:

Initial NO_3^-–N concentration (1.000 ml 0.1428 M KNO_3/200 ml)	10 ppm
Fe^{++}/NO_3^- mole ratio (2.000 ml 0.5712 M $FeSO_4$ + 0.0022 M H_2SO_4/200 ml)	8
OH^-/Fe^{++} mole ratio (1.70 ml 0.98 M NaOH/200 ml)	1.46
Reaction time	24 hours
Temperature	85 F
Atmosphere	Helium

(a) For each ppm Cu^{++} 0.200 ml 0.0157 M $CuSO_4$/200 ml was used

(b) Calculated concentration from the copper impurity in the $FeSO_4$

(c) 16.3 ppm Pb^{++} (molar equivalent of 5 ppm Cu^{++}) added as 0.0478g solid $PbSO_4$

APPENDIX VIII

EFFECT OF ORDER OF ADDITION OF CATALYST

Experiment No.	Order of Catalyst Addition[a]	pH		Reaction Time, Hours	Nitrogen Material Balance, ppm				Gaseous-N, Percent Yield
		Initial	Final		NH_3-N	NO_3^--N	NO_2^--N	Gaseous-N (By Difference)	
34	Normal	8.82	4.12	24	2.0	1.4	5.0	1.6	19
37	Normal	8.84	5.78	24	2.7	0.6	3.3	3.4	36
41	Normal	8.60	5.30	24	2.7	0.6	5.2	1.5	16
60	Last	8.80	5.69	24	2.8	2.1	2.0	3.1	39
61	Last	8.78	6.20	24	2.9	1.7	3.2	2.2	27
40	Normal	8.76	6.12	1.5	2.6	0.4	6.3	0.7	7
56	Normal	8.71	7.90	1	1.7	0.5	7.3	0.5	5
57	Normal	8.79	6.40	1	2.6	0.2	7.9	0.3	3
62	Last	8.68	8.98	1	0.4	4.7	4.9	0.0	0
63	Last	8.85	8.60	2	1.0	3.4	5.3	0.3	5

Fixed Conditions:

Initial NO_3^--N concentration (1.000 ml 0.1428 M KNO_3/200 ml)	10 ppm
Fe^{++}/NO_3^- mole ratio (1.500 ml 0.5712 M $FeSO_4$ + 0.0022 M H_2SO_4/200 ml)	6
OH^-/Fe^{++} mole ratio (1.60 ml 0.98 M NaOH/200 ml)	1.83
Catalyst concentration (1.000 ml 0.0157 M $CuSO_4$/200 ml)	5 ppm Cu^{++}
Reaction Time	24 hours
Temperature	85 F
Atmosphere	Helium

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(a) Normal addition of reagents: $FeSO_4$, $CuSO_4$, NaOH, KNO_3

APPENDIX IX

EFFECT OF RECYCLED SOLID REACTION PRODUCTS

Experiment No.	Catalyst Source	Fe^{++}/NO_3^- Ratio	OH^-/Fe^{++} Ratio	pH		Nitrogen Material Balance, ppm			
				Initial	Final	NH_3–N	NO_3^-–N	NO_2^-–N	Gaseous-N (by difference)
7	(a)	8	1.46	8.15	5.30	1.8	0.8	-0.3	7.7
8	(a)	8	1.46	8.00	5.30	1.8	0.8	0.3	6.2
9	(a)	8	1.46	8.04	5.53	1.9	0.7	0.5	6.9
58	(b)	8	1.46	8.36	5.04	3.7	1.2	0.2	4.9
59	(b)	8	1.46	8.30	5.48	3.2	1.2	-0.1	5.7
277 Q	(c)	6.5	1.23	--	--	3.1	5.7	0.9	-0.1
277 V	(d)	6.5	1.23	--	--	1.8	6.0	0.7	1.1
240	(e)	8	1.50	8.11	6.38	3.4	4.4	-0.2	2.4

Fixed Conditions:

Initial NO_3^-–N concentration (1.000 ml 0.1428 M KNO_3/200 ml)	10 ppm
Reaction time	24 hours
Temperature	85 F
Atmosphere	Helium

(a) Fresh catalyst control 1.000 ml 0.0157 M $CuSO_4$/200 ml equivalent to 5 ppm Cu^{++}

(b) Black solids equivalent to 5 ppm Cu^{++} from Experiments 56 (used in 58) and 57 (used in 59) which may be found in Appendix IV

(c) Black solids accumulated after flow reactor had run for approximately 100 hours

(d) Black solids accumulated 13 hours after cleaning without altering flowrates used for Experiment 277 Q

(e) Presumably CuO equivalent to 5 ppm Cu^{++} with FeOOH from an attempt to prepare $Cu(FeO_2)_2$

APPENDIX X

DISSOLUTION OF COPPER OR COPPER COMPOUNDS IN ACIDIC FERROUS SULFATE

Copper Source	Leaching Time, Hours	Cu^{++} Concentration, ppm
Recovered[a] Fe_3O_4	0.25	2.35
	0.50	2.05
	0.75	1.90
	1.0	1.85
	1.5	2.15
	5.0	1.90
	24.0	4.22
Recovered[b] 150 Mesh Copper Powder	0.25	0.30; 0.09[c]
	0.50	0.38; 0.13[c]
	0.75	0.41; 0.17[c]
	1.0	0.48; 0.22[c]
	1.25	0.52; 0.28[c]
	24.0	- ; 1.40[c]
	68.0	4.92; -
As-Received 150 Mesh Copper Powder	0.25	0.65; 0.30[c]
	0.50	1.35; 0.60[c]
	0.75	1.77; 0.75[c]
	1.0	2.03; 1.02[c]
	1.25	2.22; 1.23[c]
	24.0	- ; 9.55[c]
	68.0	56.4[d]; -

Fixed Conditions:

Leaching medium (2.000 ml 0.5712 M $FeSO_4$ + 0.0022M H_2SO_4/200 ml)	5.712×10^{-3}M $FeSO_4$ 2.2×10^{-5}M H_2SO_4
Temperature	85 F
Atmosphere	Helium

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(a) From experiment 271, Appendix V
(b) From experiments 262-264, Appendix XI
(c) Second leaching with fresh solution
(d) Air had leaked into reactor blackening copper and precipitating brown FeOOH

APPENDIX XI

ELEMENTAL COPPER AS CATALYST SOURCE

Experiment No.	Catalyst Form(a)	Volume 0.98M NaOH, ml	OH^-/Fe^{++} Mole Ratio	pH		Nitrogen Material Balance, ppm			
				Initial	Final	NH_3-N	NO_3^--N	NO_2^--N	Gaseous-N (by difference)
258(b)	0.2610g Shot	2.15	1.84	8.12	8.12	0.6	9.4	0.7	-0.7
259(b)	0.2554g Shot	2.15	1.84	8.26	8.11	0.9	9.5	-0.1	-0.3
260	0.2581g Shot	2.20	1.89	8.34	8.08	0.5	9.7	0.2	-0.4
261	0.2694g Shot	2.18	1.87	8.16	8.01	0.2	9.9	0.2	-0.3
262(b)	0.2207g Powder	2.12	1.82	8.10	8.15	4.7	0.5	4.5	0.3
263	0.2285g Powder	2.12	1.82	8.10	6.44	4.7	0.9	4.9	-0.5
264	0.2302g Powder	2.13	1.83	8.20	8.33	4.7	0.4	5.5	-0.6

Fixed Conditions:

Initial NO_3^--N concentration (1.000 ml 0.1428 M KNO_3/200 ml)	10 ppm
Fe^{++}/NO_3^- ratio (2.000 ml 0.5712 M $FeSO_4$ + 0.0022 M H_2SO_4/200 ml)	8
Reaction time	24 hours
Temperature	85 F
Atmosphere	Helium

(a) Calculated approximate surface area (assuming spherical particles) of No. 1 shot (0.157 cm^2) and 150 mesh powder (10.6 cm^2)

(b) Metal heated for 1 hour at 85 F with $FeSO_4$ before addition of NaOH and KNO_3

APPENDIX XII

EFFECT OF PHOSPHATE ON DENITRIFICATION USING $FeSO_4$-$CuSO_4$

Experiment No.	$PO_4^{\equiv}$ - P Concentration, ppm		Volume 0.98N NaOH, ml	OH^-/Fe^{++} Mole Ratio(a)	pH		Nitrogen Material Balance, ppm				Gaseous-N, Percent Yield
	Initial	Final			Initial	Final	NH_3-N	NO_3^--N	NO_2^--N	Gaseous-N (by difference)	
72	10	-	0.85	0.73(0.84)	8.16	6.14	0.8	9.4	0.0	-0.2	-
73	10	-	0.85	0.73(0.84)	7.98	6.36	1.2	9.4	0.9	-1.5	-
74	5	-	1.50	1.29(1.34)	8.26	6.40	1.6	7.0	0.4	1.0	33
75	5	-	1.50	1.29(1.34)	8.22	5.41	1.4	7.2	0.4	1.0	36
76	2	-	1.70	1.46(1.48)	8.03	6.55	1.3	6.2	0.6	1.9	50
77	2	-	1.70	1.46(1.48)	7.99	6.70	1.3	6.6	0.2	1.9	56
237	2	0.0	0.74	0.63(0.66)	7.25	6.06	0.5	8.7	0.0	0.8	62
238	2	0.0	0.74	0.63(0.66)	7.28	6.16	0.4	9.2	0.0	0.4	50
229	2	0.0	1.50	1.29(1.31)	7.31	5.63	1.3	6.8	0.0	1.9	59
230	2	0.0	1.50	1.29(1.31)	7.34	5.71	1.2	6.6	0.8	1.4	41
231	2	0.5	1.90	1.63(1.65)	7.78	9.14	1.8	6.3	2.1	-0.2	-
232	2	0.5	1.90	1.63(1.65)	7.65	9.16	1.5	6.2	1.3	1.0	26
235	2	0.9	2.02	1.73(1.76)	8.08	9.72	0.7	6.9	2.6	-0.2	-
236	2	0.7	2.06	1.77(1.79)	8.68	9.82	0.6	7.5	1.3	0.6	24
233	2	0.8	2.10	1.80(1.82)	9.42	9.91	0.5	8.1	1.1	0.3	16
234	2	0.7	2.10	1.80(1.82)	9.64	10.01	0.3	7.6	0.9	1.2	50
78	1	-	1.90	1.63(1.64)	8.16	8.40	1.2	5.7	0.0	3.1	72
79	1	-	1.90	1.63(1.64)	8.19	9.68	1.6	5.4	0.2	2.8	61
132[b]	1	0.1	9.70	1.66(1.66)	8.24	7.35	1.3	6.6	1.8	0.3	9
123[b]	0.5	0.1	10.00	1.72(1.72)	8.25	6.30	4.6	1.7	2.4	1.3	16
166[b]	0.5	0.0	14.00[c]	1.74(1.74)	8.30	4.94	4.3	0.1	4.1	1.5	15

Fixed Conditions:

Initial NO_3^--N concentration (1.000 ml 0.1428N KNO_3/200 ml)	10 ppm
Fe^{++}/NO_3^- mole ratio (2.000 ml 0.5712N $FeSO_4$ + 0.0022N H_2SO_4/200 ml)	8
Catalyst concentration (1.000 ml 0.0157N $CuSO_4$/200 ml)	5 ppm Cu^{++}
Initial $PO_4^{\equiv}$-P concentration (0.100 ml 0.0646M Na_2HPO_4/200 ml for each ppm)	
Reaction time	24 hours
Temperature	85 F
Atmosphere	Helium

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(a) Parenthetical value assumes 2 NaOH available from each Na_2HPO_4
(b) 1000 ml reaction volume
(c) 0.30 ml 12N HCl added to lower initial pH

APPENDIX XIII

EFFECT OF PHOSPHATE ON DENITRIFICATION USING $FeCl_2$-$CuCl_2$

Experiment No.	$PO_4^{\equiv}$-P Concentration, ppm	Volume 0.98N NaOH, ml	OH^-/Fe^{++} Mole Ratio[a]	pH		Nitrogen Material Balance, ppm				Gaseous-N, Percent Yield
				Initial	Final	NH_3-N	NO_3^--N	NO_2^--N	Gaseous-N (by difference)	
241	0	2.20	1.89	8.39	8.96	5.4	1.6	3.1	-0.1	-
242	0	2.20	1.89	8.28	9.18	5.3	0.7	4.2	-0.2	-
243	1	2.15	1.84(1.86)	8.20	8.30	5.1	1.0	3.6	0.3	3
244	1	2.15	1.84(1.86)	8.37	8.66	5.2	0.8	4.4	-0.4	-
245	2	2.10	1.80(1.82)	8.06	5.96	5.3	2.7	1.4	0.6	8
246	2	2.10	1.80(1.82)	8.22	7.45	5.1	1.6	2.8	0.5	6
247	5	2.05	1.76(1.82)	7.94	6.66	5.1	3.2	0.3	1.4	21
248	5	2.05	1.76(1.82)	7.96	8.87	1.7	5.8	0.8	1.7	40
91	0	1.80	1.54	8.29	5.59	5.5	4.3	0.0	0.2	4
92	0	1.80	1.54	8.20	5.52	5.2	4.5	0.2	0.1	2
249	0	1.50	1.29	7.75	5.65	4.3	5.4	0.0	0.3	7
250	0	1.50	1.29	7.73	5.55	4.2	5.6	0.2	0.0	0
251	1	1.50	1.29(1.30)	7.73	5.77	3.4	5.2	0.0	1.4	29
252	1	1.50	1.29(1.30)	7.86	5.89	3.5	5.0	0.0	1.5	30
253	2	1.50	1.29(1.31)	7.83	6.97	0.9	6.5	1.5	1.1	31
254	2	1.50	1.29(1.31)	7.70	7.12	0.9	6.5	0.9	1.7	49
255	5	1.50	1.29(1.34)	7.67	7.14	1.4	7.4	0.0	1.2	48
256	5	1.50	1.29(1.34)	7.75	7.04	1.4	7.5	0.0	1.1	44

Fixed Conditions:

Initial NO_3^--N concentration (1.000 ml 0.1428M KNO_3/200 ml)	10 ppm
Fe^{++}/NO_3^- mole ratio (1.000 ml 1.1424M $FeCl_2$/200 ml)	8
Catalyst concentration (1.000 ml 0.0157M $CuCl_2$/200 ml)	5 ppm Cu^{++}
Initial $PO_4^{\equiv}$-P concentration (0.100 ml 0.0646M Na_2HPO_4/200 ml for each ppm)	
Reaction time	2¼ hours
Temperature	85 F
Atmosphere	Helium

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(a) Parenthetical value assumes 2 NaOH available from each Na_2HPO_4

APPENDIX XIV

EFFECT OF ADDITIVES ON DENITRIFICATION IN THE PRESENCE OF PHOSPHATE

Experiment No.	Additive Concentration, ppm(a)	$PO_4^{=}$-P Concentration, ppm		Volume 0.98N NaOH, ml or wt CaO, mg(b)	OH^-/Fe^{++} Mole Ratio	pH		Nitrogen Material Balance, ppm				Gaseous-N, Percent Yield
		Initial	Final			Initial	Final	NH_3-N	NO_3^--N	NO_2^--N	Gaseous-N (by difference)	
82	7.5 Al^{+++}	10	-	1.60	1.37	8.16	6.80	1.2	7.9	0.4	0.5	24
83	7.5 Al^{+++}	10	-	1.60	1.37	8.04	6.66	1.1	8.2	-0.1	0.8	44
86	7.5 Al^{+++}	1	-	1.80	1.54	8.08	6.62	1.0	6.8	0.0	2.2	69
87	7.5 Al^{+++}	1	-	1.80	1.54	7.90	7.02	1.0	7.0	0.0	2.0	67
80	14.4 Fe^{+++}	10	-	1.40	1.20	8.20	6.31	0.7	7.9	0.3	1.1	52
81	14.4 Fe^{+++}	10	-	1.40	1.20	7.60	5.93	0.6	7.8	0.8	0.8	36
84	14.4 Fe^{+++}	1	-	1.90	1.63	8.10	7.50	1.1	6.6	0.2	2.1	62
85	14.4 Fe^{+++}	1	-	1.70	1.46	8.08	6.42	1.0	7.0	0.3	1.7	57
111(c)	RS 109	10	0.4	(59.9)	1.87	7.39	8.00	1.3	8.5	0.0	0.2	13
115(d)	RS 111	10	0.4	(60.2)	1.88	7.34	7.28	1.4	7.9	0.0	0.7	33
119(d)	RS 115	10	0.4	(60.2)	1.88	7.36	8.20	1.4	8.2	0.0	0.4	22
112(c)	RS 109	10	0.4	(59.9)	1.87	6.40	7.52	1.3	8.1	0.0	0.6	32
116(d)	RS 112	10	0.4	(60.5)	1.89	7.52	8.17	1.4	8.0	0.4	0.2	10
120(d)	RS 116	10	0.3	(60.0)	1.87	7.55	8.26	1.5	8.3	0.3	0.2	12
113(c,e)	RS 110	10	0.4	(59.8)	1.87	7.22	8.43	1.8	7.8	0.0	0.4	18
117(d,e)	RS 113	10	0.5	(59.7)	1.86	7.59	8.30	1.5	8.0	0.0	0.5	25
121(d)	RS 117	10	0.4	(59.7)	1.86	7.62	8.35	1.6	8.1	0.5	0.3	16
114(c,e)	RS 110	10	0.3	(60.1)	1.88	7.34	8.50	1.7	7.9	0.0	0.4	19
118(d,e)	RS 114	10	0.3	(60.3)	1.88	7.40	8.40	1.5	7.8	0.0	0.7	32
122(d,e)	RS 118	10	0.3	(60.2)	1.88	7.22	8.50	1.8	7.7	0.8	-0.3	-

Fixed Conditions:

Initial NO_3^--N concentration (1.000 ml 0.1428N KNO_3/200 ml)	10 ppm
Fe^{++}/NO_3^- mole ratio (2.000 ml 0.5712N $FeSO_4$ + 0.0022N H_2SO_4/200 ml)	8
Catalyst concentration (1.000 ml 0.0157N $CuSO_4$/200 ml)	5 ppm Cu^{++}
Reaction time	24 hours
Temperature	85 F
Atmosphere	Helium

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(a) 7.5 ppm Al^{+++} derived from 2.50 ml $Al_2(SO_4)_3$ solution analyzing 600 ppm Al; 14.4 ppm Fe^{+++} derived from 1.50 ml $Fe_2(SO_4)_3$ solution analyzing 1925 ppm Fe; RS 109 designates that one-half of the solids precipitated in experiment 109 were recycled by suspension in helium deaerated distilled water which was used as the matrix for a subsequent experiment.
(b) Parenthetical data indicates weight of solid CaO (N.F. Grade Lime) in milligrams.
(c) Order of addition of reagents: Recycled solids suspension, Na_2HPO_4, KNO_3, CaO, $FeSO_4$, $CuSO_4$.
(d) Order of addition of reagents: CaO, recycled solids suspension, Na_2HPO_4, KNO_3, $FeSO_4$, $CuSO_4$.
(e) Catalyst concentration (0.500 ml 0.0157N $CuSO_4$/200 ml); 2.5 ppm Cu^{++}.

APPENDIX XV

EFFECT OF VARIOUS PHOSPHATE REMOVAL METHODS ON DENITRIFICATION

Experiment No.	$PO_4^{\equiv}$-P Concentration, ppm		Phosphate Precipitation		Matrix	Hydroxide or (Acid)(a)		pH		Nitrogen Material Balance, ppm				Gaseous-N, Percent Yield
	Initial	Final	Source	Time, Hours		Metal	Volume, ml	Initial	Final	NH_3^--N	NO_3^--N	NO_2^--N	Gaseous-N (By Difference)	
89	10	-	80 ppm $Fe^{++}(SO_4)$	0.5	H_2O	Na	0.70	-	-	-	-	-	-	-
						Na	0.90	7.57	6.25	0.4	9.1	1.0	-0.5	-
88	10	-	80 ppm $Fe^{++}(SO_4)$+ 7.5 ppm $Al^{+++}(SO_4)$	0.5	H_2O	Na	0.70	10.10	-	-	-	-	-	-
						Na	0.90	7.92	6.30	0.6	8.8	0.0	0.6	50
A	10	-	280 ppm CaO	1	H_2O	-	-	12.04	12.04	-	10.1	-	-	-
103	-	-	-	-	A	Na	0.05	8.13	6.53	0.7	7.5	-0.1	1.9	76
104	-	-	-	-	A	Na	0.07	8.08	6.72	0.8	6.4	-0.3	3.1	86
D	10	2.0	301 ppm CaO	0.75	H_2O	-	-	-	12.01	-	9.9	-	-	-
109	2.0	0.0	-	-	D	-	-	7.78	6.99	1.2	5.9	0.0	2.9	71
110	2.0	0.0	-	-	D	-	-	7.32	7.01	1.0	6.4	0.0	2.6	72
8	10	-	560 ppm CaO	1	H_2O	-	-	12.45	12.31	-	10.1	-	-	-
105	-	-	-	-	B	-	(b)	8.10	8.00	1.2	7.2	-0.1	1.7	61
106	-	-	-	-	B	-	(b)	8.30	8.34	3.1	3.7	0.7	2.5	40
C	10	-	1120 ppm CaO	1	H_2O	-	-	12.70	12.56	-	10.1	-	-	-
107	-	-	-	-	C	-	(b)	8.10	7.56	1.1	7.3	-0.7	3.3	122
108	-	-	-	-	C	-	(b)	8.10	7.41	1.6	7.4	0.0	1.0	38
E(c)	10	0.2	46 ppm $La^{+++}(Cl)$	0.3	H_2O	Na	0.20	8.65	8.7(d)	-	9.9	-	-	-
167	0.2	0.0	-	-	E	Ca	5.50	8.13	7.24	1.3	5.3	0.0	3.4	72
168	0.2	0.0	-	-	E	Ca	5.50	8.15	7.23	0.9	5.9	0.0	3.2	78
F(c)	10	0.9	900 ppm CaO	1	H_2O(a)		(b)	9.58	-	-	9.9	-	-	-
166(f)	0.5	0.0	-	-	H_2O	Ca	14.00(g)	8.30	4.94	4.3	0.1	4.1	1.5	15
169(h)	10	6.8	¼ blk prcpt 166	0.25	H_2O		(0.07)	5.38	-	-	9.9	-	-	-
170(h)	10	6.9	¼ blk prcpt 166	0.25	H_2O		(0.07)	5.41	-	-	10.1	-	-	-
171(c)	0.9	0.2	¼ blk prcpt 166	0.25	F		(0.44)	5.13	5.37	-	9.9	-	-	-
172	6.8	0.1	-	-	169	Ca	4.00	8.37	6.38	0.9	8.7	0.5	-0.1	-
173	6.9	0.1	-	-	170	Ca	4.20	8.35	6.67	1.0	8.0	0.5	0.5	25
174	0.2	0.1	-	-	171	Ca	5.40	8.35	6.80	1.1	7.1	0.0	0.8	28
175	0.2	0.1	-	-	171	Ca	5.50	8.31	6.88	1.0	7.2	0.0	0.8	29

APPENDIX XV
(Concluded)

Experiment No.	$PO_4^{=}$-P Concentration, ppm		Phosphate Precipitation		Matrix	Hydroxide or (Acid)[a]		pH		Nitrogen Material Balance, ppm				Gaseous-N, Percent Yield
	Initial	Final	Source	Time, Hours		Metal	Volume, ml	Initial	Final	NH_3-N	NO_3^--N	NO_2^--N	Gaseous-N (By Difference)	
123[f]	0.5	0.1	-	-	H_2O	Na	10.00	8.25	6.30	4.6	1.7	2.4	1.3	16
124[h]	10	2.1	½ blk prcpt 123	1.5	H_2O	-	(0.10)	6.02	5.90	0.4	9.5	0.6	-	-
128	2.1	1.6	-	-	124	Na	1.90	8.15	8.80	1.8	6.6	0.0	1.6	47
125[h]	10	1.4	½ blk prcpt 123	1.5	H_2O	-	(0.05)	7.05	6.80	0.2	10.0	0.0	-	-
129	1.4	0.0	-	-	125	Na	1.60	8.12	6.27	1.5	7.5	0.0	1.0	40
126[h]	10	2.7	½ blk prcpt 125	1.5	H_2O	-	(trace)	7.98	7.83	0.0	10.0	0.0	-	-
130	2.7	0.0	-	-	126	Na	1.64	8.12	6.35	1.4	7.1	0.1	1.4	48
127[h]	10	2.0	½ blk prcpt 123	1.5	H_2O	Na	trace	9.00	8.46	0.0	10.5	1.4	-	-
131	2.0	0.0	-	-	127	Na	1.40	8.14	6.16	1.3	7.5	0.4	0.8	32
132[f]	1	0.1	-	-	H_2O	Na	9.70	8.24	7.35	1.3	6.6	1.8	0.3	9
133[h]	10	0.0	½ grn prcpt 132	1.5		-	(1.10)	5.53	6.11	0.2	10.1	0.0	-	-
137	0.0	0.0	-	-	133	Na	2.70	8.20	5.52	6.6	0.1	0.2	3.1	31
134[h]	10	0.0	½ grn prcpt 132	1.5		-	(1.10)	5.64	6.01	-	9.6	-	-	-
138	0.0	0.0	-	-	134	Na	2.70	8.17	-	5.7	0.1	0.2	4.0	40
135[h]	10	0.0	½ grn prcpt 132	0.25		-	(1.10)	5.66	5.63	-	9.7	-	-	-
139	0.0	0.0	-	-	135	Na	2.70	8.14	6.30	4.8	0.1	0.0	5.1	51
136[h]	10	0.0	½ grn prcpt 132	0.25		-	(1.10)	5.68	5.62	0.0	9.7	-	-	-
140	0.0	0.0	-	-	136	Na	2.70	8.14	5.75	6.3	0.1	0.4	3.2	32
141	10	2.5	blk prcpt 140	2	H_2O	-	(1.10)	2.28	2.31	-	-	-	-	-
142	10	1.9	blk prcpt 137	2	H_2O	-	(1.10)	2.28	2.40	-	-	-	-	-
143	10	7.1	blk prcpt 138	6S[i]	H_2O	-	(1.10)	2.31	2.38	-	-	-	-	-
144	10	4.5	blk prcpt 139	6S[i]	H_2O	-	(1.10)	2.25	2.40	-	-	-	-	-

Fixed Conditions:

Initial NO_3^--N concentration (1.000 ml 0.1428N KNO_3/200 ml)	10 ppm
Fe^{++}/NO_3^- mole ratio (2.000 ml 0.5712N $FeSO_4$ + 0.0022N H_2SO_4/200 ml or 1.833 ml 0.5712N $FeSO_4$ + 0.0022N H_2SO_4 and 0.083 ml 1.1424N $FeCl_2$/200 ml)	8
Catalyst concentration (1.000 ml 0.0157N $CuSO_4$/200 ml)	5 ppm Cu^{++}
Initial $PO_4^{=}$-P concentration (0.100 ml 0.0640N Na_2HPO_4/200 ml for each ppm)	
Reaction time	24 hours
Temperature	85 F
Atmosphere	Helium

(a) 0.98N NaOH, 1 percent $Ca(OH)_2$ slurry (equivalent to 0.134N), or 0.5N H_2SO_4
(b) pH adjusted with unmeasured volume of 6N H_2SO_4
(c) 500 ml reaction volume
(d) pH varied from 8.49-8.89 with helium flowrate
(e) Solution contained 0.10247g $Na_2CO_3 \cdot H_2O$ (100 ppm $CO_3^=$)
(f) 1000 ml reaction volume
(g) 0.39 ml 12N HCl added to lower initial pH
(h) 250 ml reaction volume
(i) Air bubbled through reaction mixtures

APPENDIX XVI

EFFECT OF CARBONATE ON DENITRIFICATION

Experiment No.	$CO_3^{=}$ Concentration, (a) ppm	OH^-/Fe^{++} Mole Ratio	pH		Reaction Time, Hours	Nitrogen Material Balance, ppm				Gaseous-N, Percent Yield
			Initial	Final		NH_3-N	NO_3^--N	NO_2^--N	Gaseous-N (By Difference)	
(b)	100	-	10.3	10.2	24	3.5	1.8	4.3	0.4	5
(b)	100	-	9.0	8.4	24	4.4	3.2	1.8	0.6	9
28	100(c)	1.46(1.75)(d)	8.20	6.84	24	3.2	0.6	1.0	5.2	55
178	100	1.40	8.06	6.64	24	2.4	2.8	0.4	4.4	61
179	100	1.40	8.11	6.78	24	2.6	2.8	0.1	4.5	63
184	100	1.40	8.08	6.22	48	3.0	2.5	0.5	4.0	53
185	100	1.40	8.07	6.33	48	2.9	2.2	0.5	4.4	56
180	200	1.40	8.15	7.14	24	0.8	7.4	0.5	1.3	50
181	200	1.40	8.04	7.30	24	1.2	4.7	0.0	4.1	77
186	200	1.40	8.11	7.10	48	1.2	7.6	0.3	0.9	38
187	200	1.40	8.23	7.15	48	1.2	7.3	0.9	0.6	22
182	300	1.40	8.18	7.25	24	0.7	8.4	-0.1	1.0	63
183	300	1.40	8.17	7.33	24	0.5	8.4	0.4	0.7	44
188	300	1.40	8.14	7.27	48	0.7	8.0	0.3	1.0	50
189	300	1.40	8.13	7.25	48	0.7	8.4	0.4	0.5	31

Fixed Conditions:

Initial NO_3^--N concentration (1.000 ml 0.1428M KNO_3/200 ml)	10 ppm
Fe^{++}/NO_3^- mole ratio (2.000 ml 0.5712M $FeSO_4$ + 0.0022M H_2SO_4/200 ml)	8
Catalyst concentration (1.000 ml 0.0157M $CuSO_4$/200 ml)	5 ppm Cu^{++}
$CO_3^{=}$ concentration (1.00 ml 0.3333M $NaHCO_3$/200 ml for each 100 ppm)	
pH adjustment (6.40 ml 1 percent $Ca(OH)_2$ slurry)	
Temperature	85 F
Atmosphere	Helium

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(a) Carbonate added after iron and copper salts
(b) Data from feasibility study (Gunderloy, 1968) where 0.3333M K_2CO_3 and 6M NaOH solutions were used.
(c) 1.00 ml 0.3334M Na_2CO_3/200 ml initially of which 66 percent remained in solution after 24 hours.
(d) pH adjusted with 1.70 ml 0.98M NaOH; parenthetical value assumes 1 NaOH available for each Na_2CO_3.

APPENDIX XVII

EFFECT OF BASE-BOROSILICATE GLASS CONTACT TIME ON DENITRIFICATION

Experiment No.	NaOH Age, Days	pH		Nitrogen Material Balance, ppm				Gaseous-N, Percent Yield
		Initial	Final	NH_3-N	NO_3^--N	NO_2^--N	Gaseous-N (By Difference)	
22	0	7.90	4.35	1.9	0.8	0.7	6.6	71
23	0	7.80	5.35	1.9	0.6	0.4	7.1	76
24	0	8.08	4.25	2.0	0.6	0.5	6.9	73
25	0	7.87	5.61	1.9	1.1	0.1	6.9	78
26	0	7.59	5.11	2.1	1.2	0.2	6.5	74
28	0[a]	8.20	6.84	3.2	0.6	1.0	5.2	55
7	7	8.15	5.30	1.8	0.8	-0.3	7.7	84
8	7	8.00	5.30	1.8	0.7	0.3	7.2	77
9	7	8.04	5.53	1.9	0.7	0.5	6.9	74
16	28	8.27	7.24	1.9	2.9	0.7	4.5	63
17	50	8.28	7.30	1.1	5.0	0.0	3.9	78
18	55	8.10	6.81	1.6	4.9	0.3	3.2	63
27	71	7.82	7.44	0.9	4.4	0.3	4.4	79

Fixed Conditions:

Initial NO_3^--N concentration (1.000 ml 0.1428M KNO_3/200 ml)	10 ppm
Fe^{++}/NO_3^- mole ratio (2.000 ml 0.5712M $FeSO_4$ + 0.0022M H_2SO_4/200 ml)	8
Catalyst concentration (1.000 ml 0.0157M $CuSO_4$/200 ml)	5 ppm Cu^{++}
OH^-/Fe^{++} mole ratio (1.70 ml 0.98M NaOH)	1.46
Reaction time	24 hours
Temperature	85 F
Atmosphere	Helium

(a) Stored 6 days in polyethylene

APPENDIX XVIII

PRECIPITATION OF SILICA WITH ALUMINUM, CUPRIC, OR FERRIC SULFATES

Precipitant	M/Si Mole Ratio	Initial pH	SiO_2 Remaining In Solution, ppm	SiO_2 Precipitated, percent
$Al_2(SO_4)_3$	2	4.03	22.4	7.8
		5.05	18.5	23.9
		5.93	14.9	38.7
		6.93	9.4	61.3
		7.60	5.8	76.1
		7.80	6.2	74.5
		8.00	4.9	79.8
		8.20	4.7	80.7
		9.01	19.0	21.8
		10.01	23.8	2.1
		11.00	23.9	1.6
$CuSO_4$	1	3.94	23.8	2.1
		4.93	23.1	4.9
		6.19	23.4	3.7
		6.99	18.0	25.9
		8.03	18.0	25.9
		9.00	17.9	26.3
		10.02	18.2	25.1
		10.98	19.6	19.3
$Fe_2(SO_4)_3$	2	3.96	21.2	12.8
		5.05	19.4	20.2
		5.96	16.2	33.3
		6.93	12.7	47.7
		8.03	12.1	50.2
		8.99	16.0	34.2
		9.97	16.3	32.9

Fixed Conditions:

Initial SiO_2 concentration (50.0 ml solution obtained by 20-fold dilution of 0.0162 M Na_2SiO_3/100 ml)	24.3 ppm
Reaction time	1 hour
Temperature	85 F
Atmosphere	Helium

APPENDIX XIX

EFFECT OF SILICA ON DENITRIFICATION

Experiment No.	SiO_2 Concentration, ppm		Volume 0.98 M NaOH, ml	OH^-/Fe^{++} Mole Ratio	pH		Nitrogen Material Balance, ppm				Gaseous-N, Percent Yield
	Initial	Final			Initial	Final	NH_3-N	NO_3^--N	NO_2^--N	Gaseous-N (by difference)	
219	0	(a)	2.00	1.72	8.50	3.96	4.6	1.1	4.2	0.1	1
220	0	0.9	1.95	1.67	8.25	5.02	3.9	0.8	0.5	4.8	52
221	1.0	1.4	1.90	1.63	8.07	5.27	3.6	0.5	1.1	4.8	51
222	1.0	1.4	1.95	1.67	7.94	5.59	4.1	0.5	0.5	4.9	52
223	4.9	3.5	1.90	1.63	8.13	5.37	4.6	1.3	0.8	3.3	38
224	4.9	3.1	1.95	1.67	8.05	5.40	4.7	0.8	1.0	3.5	38
225	9.7	5.0	1.95	1.67	8.23	5.82	4.8	1.8	1.5	1.9	23
226	9.7	3.8	2.00	1.72	8.25	6.39	4.8	0.6	3.4	1.2	13
227	19.4	5.6	1.85	1.59	8.13	6.59	4.9	3.6	0.4	1.1	17
228	19.4	7.3	1.92	1.65	8.31	6.66	4.4	2.8	1.9	0.9	13

Fixed Conditions:

Initial NO_3^--N concentration (1.000 ml 0.1428 M KNO_3/200 ml)	10 ppm
Fe^{++}/NO_3^- mole ratio (2.000 ml 0.5712 N $FeSO_4$ + 0.0022 M H_2SO_4/200 ml)	8
Catalyst concentration (1.000 ml 0.0157 M $CuSO_4$/200 ml)	5 ppm Cu^{++}
Initial Silica concentration (1.00 ml 0.0162 M Na_2SiO_3/200 ml for each 4.9 ppm SiO_2)	
Reaction time	24 hours
Temperature	85 F
Atmosphere	Helium

APPENDIX XX

UNCATALYZED REDUCTION OF NITRITE

Experiment No.	Volume 0.98N NaOH, ml	OH^-/Fe^{++} Mole Ratio	pH[a] Initial	pH[a] Final	Reaction Time, Hours	Nitrogen Material Balance, ppm NH_3-N	NO_3^--N	NO_2^--N	Gaseous-N (by difference)	Gaseous-N, Percent Yield
265	1.05	1.82	8.12	8.60	24	4.3	0.0	5.9	-0.1	-
266	1.05	1.82	8.40	8.35	24	4.2	0.1	5.9	-0.2	-
267	0.80	1.38	7.90	5.85	24	1.3	0.0	0.3	8.5	8.7
268	0.80	1.38	7.85	5.96	24	1.5	0.1	0.0	8.5	8.4
278	0.80	1.38	8.57	5.31	24	1.4	0.1	0.6	7.9[b]	8.3
279	0.80	1.38	8.42	4.98	24	1.2	0.0	0.5	8.3[b]	8.6
269	0.60	1.04	7.60	5.95	24	1.0	0.1	0.7	8.3	8.8
270	0.60	1.04	7.62	4.11	24	1.0	0.1	1.3	7.7	8.8
272[c,d]	4.00	1.38	7.60	7.24	0.5	1.1	0.0	7.0	2.0	65
				7.39	1	1.2	0.0	6.5	2.4	67
				7.40	2	1.2	0.0	4.8	4.1	77
				7.51	3	1.2	0.0	1.1	7.8	87
				6.24	4	1.3	0.1	0.5	8.2	85
				6.02	5	1.3	0.1	0.0	8.7	86
				5.98	24	1.4	0.1	0.0	8.6	85
274[c]	4.00	1.38	7.70	7.80	0.5	0.2	0.0	8.7	1.2	86
				7.46	1	0.3	0.0	8.2	1.6	84
				6.94	2	0.6	0.1	6.0	3.4	83
				7.08	3	0.6	0.1	4.5	4.9	88
				7.04	4	0.7	0.1	3.4	5.9	88
				6.01	7.5	0.8	0.1	0.8	8.4	90
				4.90	23	0.9	0.0	0.0	9.2	91
275[c,e]	4.00	1.38	7.52	7.20	0.5	0.4	0.1	4.8	4.7	90
				7.14	1	0.5	0.0	4.8	4.7	90
				7.20	2	0.5	0.0	5.0	4.5	90
				7.30	3	0.5	0.0	5.1	4.4	90
				7.34	4	0.5	0.0	5.3	4.2	89

Fixed Conditions:

Initial NO_2^--N concentration (10.0 ml 0.0144N $NaNO_2$/200 ml)	10.1 ppm
Fe^{++}/NO_2^- mole ratio (1.000 ml 0.5712N $FeSO_4$ + 0.0022N H_2SO_4/200 ml)	4
Temperature	85°F
Atmosphere	Helium

(a)With the exception of experiments 278 and 279 the pH values are suspected to be low due to a failing electrode.
(b)Analysis for hydroxylamine in experiments 278 and 279 gave -0.01 and 0.01 ppm NH_2OH-N, respectively.
(c)1000 ml reaction volume.
(d)NaOH added last.
(e)Initial NO_2^--N concentration, 10.0 ppm; initial $PO_4^{\ominus}$-P concentration, 1 ppm (0.500 ml 0.0646N Na_2HPO_4/1000 ml)

APPENDIX XXI

EFFECT OF REACTION TIME ON DENITRIFICATION

Experiment No.	Fe^{++}/NO_3^- Mole Ratio	Volume 0.98N NaOH, ml/1000 ml	OH^-/Fe^{++} Mole Ratio	pH		Reaction Time, Hours	Nitrogen Material Balance, ppm				Gaseous-N, Percent Yield
				Initial	Final		NH_3-N	NO_3^--N	NO_2^--N	Gaseous-N (by difference)	
273A	6	6.00	1.37	7.40	7.05	0.5	0.4	5.8	3.5	0.3	7
B					7.06	1	0.5	5.8	3.5	0.2	5
C					7.34	2	0.5	5.5	0.8	3.2	71
D					5.72	3	0.8	4.4	0.8	4.0	71
E					5.45	4	0.8	4.0	0.4	4.8	80
F					5.48	5	0.8	3.9	0.3	5.0	82
G					5.20	24[a]	0.8	3.9	0.0	5.3	87
H					7.04	29	0.8	3.8	0.0	5.4	87
239A[b]	8[d]	8.50	1.46[c]	9.4	7.55	1	0.1	8.6	1.2	0.1	7
B					7.6	2	0.4	7.8	1.0	0.8	36
C					7.6	3	1.1	6.7	1.3	0.9	27
D					7.6	4	1.9	5.6	1.3	1.2	27
E					7.6	5	2.4	5.3	0.6	1.7	36
F					7.5	6	2.8	4.4	2.3	0.5	9
G					7.0	7	2.8	4.4	0.7	2.1	37
H					4.05	24	3.0	4.5	1.9	0.6	11
257A[b]	8[d]	10.50	1.80[c]	5.68	7.64	1	0.1	8.7	0.7	0.5	38
B					7.80	2	0.6	7.0	2.4	0.0	0
C					7.84	3	1.4	5.0	3.1	0.5	10
D					7.78	4	2.6	4.5	2.0	0.9	20
E					7.69	5	3.1	3.8	2.7	0.4	6
F					6.91	6	3.3	3.8	1.6	1.3	21
G					5.74	24	3.4	3.4	-0.1	3.3	50

Fixed Conditions:

Initial NO_3^--N concentration (5.000 ml 0.1428M KNO_3/1000 ml)	10 ppm
Final Fe^{++}/NO_3^- mole ratio (1.25 ml 0.5712M $FeSO_4$ + 0.0022M H_2SO_4/1000 ml for each unit value of ratio)	
Final catalyst concentration (5.000 ml 0.0157M $CuSO_4$/1000 ml)	5 ppm Cu^{++}
Temperature	85°F
Atmosphere	Helium

(a) Immediately after withdrawal of analytical sample 2.00 ml 0.3333M $NaHCO_3$ was added to residual 300 ml of reaction mixture to raise pH to 6.52 (133 ppm $CO_3^=$).

(b) All nitrogen analyses normalized to 10 ppm N.

(c) In these experiments the indicated volumes of stock solutions were diluted to 100 ml and added at 25 ml/hr through a mixing chamber to an initial 950 ml of dilute KNO_3 solution: 8.50 ml (Experiment 239) or 10.50 ml (Experiment 257) of 0.98N NaOH in 100 ml; 10.000 ml 0.5712M $FeSO_4$ + 0.0022M H_2SO_4 and 5.000 ml 0.0157M $CuSO_4$ in 100 ml.

(d) Final mole ratio assuming reagents had been added to reaction mixtures to give final volume of 1000 ml.

APPENDIX XXII

DENITRIFICATION IN A FLOW REACTOR WITH RECIRCULATING SOLIDS

Experiment No.	Total Flowrate, ml/hr	Retention Time, hours	Relative Flowrates, KNO_3	$FeSO_4$-$CuSO_4$	NaOH	Elapsed Time at Steady Flow, hours	NO_3-N, ppm	Fe^{++}/NO_3^- Mole Ratio	OH^-/Fe^{++} Mole Ratio	Nitrogen Material Balance, ppm NH_3-N	NO_3^--N	NO_2^--N	Gaseous-N (by difference)	Gaseous-N, percent yield
276A[a]	113	4.1	110	(b)	(b)	5.25	9.7	(b)	(b)	2.0	5.3	2.0	0.4	0
B						17				0.7	8.8	0.0	0.2	22
C						22.33				0.7	9.2	0.9	-1.1	-
D						24.5				0.7	9.3	0.2	-0.5	-
E						41				0.7	8.6	0.0	0.4	36
F						49.5				1.7	8.2	0.0	-0.2	-
277A[c]	122	3.8	23.5	29.5	29.0	11	8.6	6.0	1.70	3.2	4.9	2.0	-1.5	-
B						12				2.6	5.2	1.4	-0.6	-
C						13				2.4	5.6	0.2	0.4	13
D						14				2.3	5.4	1.2	-0.3	-
E						15				2.3	5.5	0.9	-0.1	-
F						16				2.5	5.5	0.9	-0.3	-
G						17				2.3	54.	1.1	-0.2	-
H	58	8.0	16.5	13.5	13.5	15.5	11.4	4.9	1.38	3.2	5.8	1.1	1.3	23
I						18.5				2.9	6.2	1.1	1.2	23
J						20.5				2.8	6.4	0.7	1.5	30
K						22.5				3.0	6.4	1.1	0.9	18
L	57	8.2	5.5	8.0	11.0	11	6.7	8.8	1.90	2.4	0.6	1.8	1.9	31
M	56	8.3	8.5	11.0	8.5	10.5	9.1	7.8	1.07	3.4	3.9	1.3	0.5	10
N						12.5				3.3	4.5	0.3	1.0	22
O	69	6.7	21.0	23.5	21.0	21	9.6	6.7	1.23	3.4	5.3	0.3	0.6	14
P						23				3.2	5.5	0.4	0.5	12
Q						25				3.1	5.7	0.9	-0.1	-
R	90	7.8				6.5				0.2	2.0	0.6	6.8	89
S						8				0.3	3.5	0.6	5.2	85
T						9.75				0.6	4.6	0.7	3.7	74
U	55	8.5				11.5				1.2	5.6	0.2	2.6	65
V						13				1.8	6.0	0.7	1.1	31

Fixed Conditions:
Temperature 85 F
Atmosphere Helium

(a) Reagents: 0.5781g KNO_3 in 8000 ml = 0.0007147N KNO_3 (10 ppm NO_3^--N)
75 ml 0.5712N $FeSO_4$ + 0.0022N H_2SO_4 in 125 ml = 0.3427N $FeSO_4$ + 0.0013N H_2SO_4
60 ml 0.988N NaOH in 125 ml = 0.474N NaOH

(b) Combined $FeSO_4$ and NaOH flow was 3 to 4 percent of total flow but due to numerous mechanical problems flowrates were not sufficiently steady to provide meaningful calculation of relative flowrates or mole ratios of reagents.

(c) Reagents: 1.5159g KNO_3 in 7000 ml = 0.002142N KNO_3 (30 ppm NO_3^--N)
25.0107g $FeSO_4 \cdot 7H_2O$ + 0.4124g $CuSO_4 \cdot 5H_2O$ + 0.735 ml 0.474N H_2SO_4 in 7000 ml = 0.01290N $FeSO_4$ + 0.0002360N $CuSO_4$ + 0.0000497N H_2SO_4
126 ml 0.988N NaOH in 7000 ml = 0.0178N NaOH

APPENDIX XXIII

DENITRIFICATION IN A TUBULAR FLOW REACTOR

Experiment No.	Total Flowrate, ml/hr	Retention Time, hours	Relative Flowrates		Flowrates, ml/hr		Initial pH	NO_3^--N, ppm	Fe^{++}/NO_3^- Mole Ratio	OH^-/Fe^{++} Mole Ratio	Nitrogen Material Balance, ppm				Gaseous-N, percent yield
			KNO_3	$CuSO_4$	$FeSO_4$	NaOH					NH_3-N	NO_3^--N	NO_2^--N(a)	Gaseous-N (by difference)	
280A(b)	70	0.86	80	20	3.30	3.72	8.3 - 9.4	9.8	2.57	1.95	0.3	9.3	--	--	--
B	69	0.88	76	19.5			8.3 - 9.4	9.7	2.62	1.95	0.5	8.4	1.7	-0.9	--
C	75	0.81	80	20	3.86	3.73	7.5 - 8.1(c)	9.8	2.76	1.67	0.1	9.1	1.5(0.4)	-0.9(0.2)	--(29)
D	77	0.79					7.7 - 7.8	10.0	2.73	1.67	0.3	9.3	0.0(0.1)	0.4(0.3)	57(43)
E			83	21			7.5 - 7.6	9.8	2.73	1.67	0.2	9.3	1.3(0.1)	-1.0(0.2)	--(40)
F(d)					3.61	3.61	8.2 - 8.7	9.8	5.11	1.73	0.2	7.2	0.5	1.9	73
G	98	0.62					8.6 - 10.2	10.0	3.91	1.73	0.3	6.8	1.1	1.8	56
H					3.53	3.85	8.6 - 9.0	10.0	3.83	1.89	0.3	7.0	1.4	1.3	43
I			70	13			8.8 - 10.2	10.3	4.63	1.89	0.6	6.7	1.9	0.8	22
J							8.7 - 10.2	10.3	4.63	1.89	0.8	6.4	2.3	0.8	21
K	76	0.80					9.1 - 10.4(e)	10.3	4.63	1.89	1.0	6.6	2.3	0.4	11

Fixed Conditions:

Temperature 85 F
Atmosphere Helium

(a) Parenthetical values obtained by reduction to NH_3 rather than spectrophotometrically.

(b) Reagents (280 A-E): 0.5898g KNO_3 in 6000 ml = 0.000972M KNO_3 (13.6 ppm NO_3^--N)
0.3944g $CuSO_4 \cdot 5H_2O$ in 4000 ml = 0.000395M $CuSO_4$ (25.1 ppm Cu^{++})
3.000 ml 0.5712M $FeSO_4$ + 0.0022M H_2SO_4 in 45 ml = 0.03808 $FeSO_4$ + 0.00015M H_2SO_4
3.00 ml 0.989M NaOH in 45 ml = 0.0659M NaOH

(c) Effluent pH = 6.40

(d) Reagents (280 F-K): KNO_3 and $CuSO_4$ unchanged
$FeSO_4$ and NaOH concentrations doubled

(e) Effluent pH = 7.55

APPENDIX XXIV

DENITRIFICATION IN TAP WATER AND SECONDARY EFFLUENT SUBSEQUENT TO REMOVAL OF SILICATE AND/OR CARBONATE AND PHOSPHATE

Experiment No.	Type of Matrix[a]	Anion Removal Process[b]	Volume 1% $Ca(OH)_2$, ml	pH		Initial NO_3^--N Concentration, ppm[c]	Fe^{++}/NO_3^- Mole Ratio	Nitrogen Material Balance, ppm				Gaseous-N, Percent Yield	$PO_4^{\equiv}$-P Concentration, ppm	
				Initial	Final			NH_3-N[d]	NO_3^--N	NO_2^--N[d]	Gaseous-N (by difference)		Initial[e]	Final
176	Effluent	A	5.45	8.43	7.65	15.9	5.03	6.2(0.7)	14.1	0.0	1.1	61	0.7	0.2
177	Effluent	A	5.45	8.41	7.69	15.9	5.03	6.3(0.8)	13.9	0.0	1.2	60	0.7	0.0
190	Effluent	A	3.80	8.27	7.18	12.1	7.92	0.6(0.4)	11.0	0.0	0.7	63	0.8	0.0
191	Effluent	A	5.20	8.25	6.18	12.1	7.92	0.4(0.2)	11.5	0.0	0.4	67	0.8	0.0
192	Effluent	B	4.50	8.25	6.89	12.1	7.92	0.3(0.1)	11.4	1.8	-1.2	--	0.5	0.0
193	Effluent	B	7.20	8.31	6.91	12.1	7.92	0.9(0.7)	10.0	-0.4	1.8	86	0.5	0.0
194	Effluent	C	7.60	8.30	6.97	12.2	7.88	1.0(0.9)	11.0	0.0	0.3	25	6.9	0.0
195	Effluent	C	8.20	8.23	7.06	12.2	7.88	0.6(0.5)	10.6	0.0	1.1	69	6.9	0.0
196	Effluent	D	7.30	8.34	7.10	12.0	8.02	1.7(1.6)	8.6	0.0	1.8	53	0.9	0.0
197	Effluent	D	8.30	8.29	7.25	12.0	8.02	1.4(1.3)	9.3	0.0	1.4	52	0.9	0.0
200	Effluent	E	8.00	8.20	6.89	12.1	8.02	1.5(1.4)	8.8	0.0	1.9	58	0.2	0.0
201	Effluent	E	8.00	8.18	6.78	12.1	8.02	1.5(1.4)	8.8	0.0	1.9	58	0.2	0.0
202	Effluent	E	8.00	8.09	6.82	12.1	8.02	1.5(1.4)	8.7	0.0	2.0	59	0.1	0.0
207	Tap	None	8.20	8.35	7.35	10.2	7.82	1.5	7.6	0.0	1.1	42	0.04	0.00
208	Tap	F	10.00	8.07	6.66	10.2	7.82	2.4	5.0	0.0	1.7	33	--	--
205	Tap	A	7.40	8.24	7.57	10.2	7.82	1.6	7.4	-0.3	1.5	54	0.00	0.00
206	Tap	G	7.30	8.14	7.37	10.2	7.82	1.5	7.5	0.5	0.7	26	0.00	--
210	Tap	G	8.00	8.39	7.36	10.2	7.82	4.3	4.4	0.0	1.5	26	0.00	0.00
209	Effluent	H	9.40	8.34	9.00	10.8	8.16	3.6(2.7)	5.9	0.5(0.0)	2.7	50[f]	0.02	0.00
203	Effluent	A	6.00	8.11	7.59	10.8	8.16	2.1(1.2)	9.0	1.1(0.6)	0.5	23[f]	0.06	0.00
204	Effluent	G	6.20	8.15	7.18	10.8	8.16	1.8(0.9)	8.7	1.1(0.6)	1.1	44[f]	0.18	--
211	Effluent	G	8.20	8.38	7.90	10.8	8.16	1.7(0.8)	10.3	0.5(0.0)	0.2	20[f]	0.05	0.00
212[g]	Distilled	None	10.00	8.36	6.54	10	8.00	1.5	6.2	0.9	1.4	37	1	0.00
215[h]	From 207	I	1.60	8.40	7.20	10.0	8.00	2.3(0.8)	7.3	0.0	1.9	70	0.00	--
214[h]	From 205	I	3.20	8.32	6.38	10.0	8.00	4.3(2.7)	3.3	1.8	2.5	37	0.00	--
216[h]	From 210	I	3.60	8.40	7.68	10.0	8.00	5.5(1.2)	5.9	0.0	2.9	71	0.00	--
213[h]	From 203	I	2.60	8.38	6.87	10.0	8.00	3.0(0.7)	6.6	1.1(0.5)	2.6	63[f]	0.00	--
217[h]	From 211	I	3.00	8.33	7.01	10.3	7.76	2.6(0.9)	4.6	0.5	4.3	75	0.00	--
218[h]	From 212	I	3.40	8.36	(i)	10.0	8.00	--	--	--	--	--	0.00	--

APPENDIX XXIV

(Concluded)

Fixed Conditions:

Catalyst Concentration (1.000 ml 0.0157M $CuSO_4$/200 ml)	5 ppm Cu^{++}
Reaction Time	24 hours
Temperature	85 F
Atmosphere	Helium

(a) Effluent analysis (ppm N): NO_3^- 5.8 (experiments 176 and 177), 12.1 (experiments 190 through 197, 200 through 202), 10.8 (experiments 203, 204, 209, and 211); NO_2^- 0.5 (experiments 203, 204, 209, and 211).

(b) A--10.0 ml 1-percent $Ca(OH)_2$ slurry/1000 ml for 15 minutes at 85 F (final pH = 9.53) followed by centrifugation (for experiments 176 and 177); 6.0 ml 1-percent $Ca(OH)_2$ slurry/1000 ml for 15 minutes at 85 F (final pH = 9.75) followed by centrifugation (for experiments 190 and 191); 8.3 ml 1-percent $Ca(OH)_2$ slurry/1000 ml for 30 minutes at ambient (final pH = 9.96) followed by centrifugation (experiment 205); 10.8 ml 1-percent $Ca(OH)_2$ slurry/1000 ml for 30 minutes at ambient (pH = 9.97) followed by centrifugation (experiment 203)

B--6.0 ml 1-percent $Ca(OH)_2$ slurry/1000 ml for 15 minutes at 85 F, centrifugally clarified, 0.88 ml $Fe_2(SO_4)_3$ (analyzing 1925 ppm Fe^{++})/1000 ml during 1 hour at 85 F (final pH = 9.48) followed by centrifugation

C--0.86 ml $Fe_2(SO_4)_3$ (analyzing 1925 ppm Fe^{++})/1000 ml during 1 hour at 85 F (final pH = 8.17) followed by centrifugation

D--0.86 ml $Fe_2(SO_4)_3$ (analyzing 1925 ppm Fe^{++})/1000 ml during 1 hour at 85 F, centrifugally clarified, 6.0 ml 1-percent $Ca(OH)_2$ slurry/1000 ml for 15 minutes at 85 F (final pH = 9.51) followed by centrifugation.

E--1 ml 0.5M H_2SO_4/1000 ml (pH = 7.06), 0.98 ml $Fe_2(SO_4)_3$ (analyzing 1925 ppm Fe^{++})/1000 ml during 1 hour at 85 F (pH = 7.03), centrifugally clarified, 6.0 ml (experiment 200) or 9.2 ml (experiment 201) or 12.4 ml 1-percent $Ca(OH)_2$ slurry/1000 ml for 15 minutes at 85 F (final pH = 9.60, 10.05, and 10.55, respectively) followed by centrifugation

F--3.2 ml 0.5M H_2SO_4/1000 ml, bubbled helium for 1 hour at ambient, and added 1.2 ml more acid

G--8.3 ml (for tap) or 10.8 ml (for effluent) 1-percent $Ca(OH)_2$ slurry/1000 ml for 30 minutes at ambient (pH = 9.96), centrifugally clarified, added 0.0380 ±0.0005g MgO (~150 ppm) for 15 minutes at ambient (experiments 204 and 206) or 90 C (experiments 210 and 211) followed by centrifugation

H--4.0 ml 0.5M H_2SO_4/1000 ml, bubbled helium for 1 hour at ambient, 12.0 ml $Ca(OH)_2$ slurry/1000 ml for 15 minutes at ambient (pH = 10.95), centrifugally clarified, and added 0.4 ml more acid

I--Solutions from indicated experiment reused (after adjusting NO_3^- concentration)

(c) Includes that already present plus added KNO_3

(d) Parenthetical values refer to ammonia or NO_2^- ion formed in the denitrification process only while the other numerical values include that present in the solution initially

(e) Subsequent to the preliminary anion removal process. The samples of secondary effluent analyzed 8.9 ppm $PO_4^{\equiv}$-P (used for experiments 176 and 177, 190 through 197, and 200 through 202), and 10.9 ppm $PO_4^{\equiv}$-P (used for experiments 203 and 204, 209, 211, 213, and 217)

(f) Yield based on conversion of sum of initial NO_3^- + NO_2^-

(g) 250 ml reaction volume with 0.125 ml 0.0646M Na_2HPO_4 (1 ppm $PO_4^{\equiv}$-P), 1.25 ml 0.3333M $NaHCO_3$ (100 ppm $CO_3^{=}$), and 0.15 ml 0.5M H_2SO_4 added

(h) 100 ml reaction volume

(i) Reaction vessel broke during run